A STUDY OF THE EFFECT OF VACUUM AND PRESSURE APPLIED TO DIFFERENTIAL THERMAL ANALYSIS

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by

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FOREWARD

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ABSTRACT

The object of these investigations was to study the effects of the application of vacuum to the process of differential thermal analysis. Special interest was to be focused on the effects that vacuum application would have on the problem of organic matter in clays. It was reasoned that evacuation of the air from the combustion tube wherein thermal analysis was conducted would eliminate the oxygen therein present and as a result should reduce or eliminate the thermal reactions associated with the oxidation of the carbonaceous material. Dependent upon the amount of organic matter present in the test clay sample is the thermal reaction associated with it. Small amounts of organic matter produce thermal reactions sufficient to mask or eliminate the reactions characteristic of clay minerals present and thereby hinder or make altogether impossible their identification by thermal analysis. Accepted practice is to remove any suspected organic material from clay samples by chemical treatment with oxidizing agents. This process is not entirely satisfactory in that it does not in all cases completely remove the organic material and through the process of base exchange may change the nature of the clay fraction of the soil .

Tests conducted in vacuum were found to be unreliable, erratic and not reproducible. Some indication was derived from thermal curves produced that the method would be feasible if certain equipment were changed and a more elaborate vacuum system were employed.

Unreliability of the thermal curves produced under vacuum operation initiated, what seemed to be, the logical substitute

use of an inert atmosphere in place of vacuum. Positive test results were gained both through the use of helium and nitrogen. The shape and magnitude of the thermal reactions of natural clay samples were uneffected by thermal analysis under inert gasses when compared to those produced under atmospheric conditions. Tests were run on two natural clay samples mixed separately with five different organic materials. In addition, one natural clay sample known to contain organic material was tested. Comparison curves of the clay samples containing known amounts of carbonaceous matter showed that the thermal reaction due to oxidation of the organic material which was prevalent when tested in atmosphere was eliminated when tested in an atmosphere of inert gas.

Results of these tests imply that the technique of thermal analysis when conducted in an atmosphere of an inert gas performs the same function as does the chemical treatment of organic material by oxidizing agents. In all tests performed the removal of the organic thermal reaction was complete, the thermal reactions of the natural clays were unchanged, and the material tested was that which was originally supplied, unchanged by pretreatment with chemical oxidizing agents. This technique could be a useful addition to the proper analysis of clay minerals by differential thermal analysis.

PART I

INTRODUCTION

A. Historical Review

In the correct solution of foundation problems a proper analysis of type and properties of the soil underlying the foundation must be made. The Earth's great man-made structures would be an impossibility were it not for the strength of the soil underlying and its correct evaluation by the engineers who designed and built the structures.

In the determination of soil properties, a correct identification of the soil type is, of course, of the essence. It is with the identification of the soil material that differential thermal analysis deals where it has been adapted advantageously to the study of clay minerals.

Among the soil types it is the clay fraction of the soil which is the "bad actor" and its use as foundation material requires extreme care, good judgement and proper evaluation by the soils engineer. In the broad classification of clay material there are many groups and individual minerals whose peculiarities of crystalline structure and physical properties set them apart from other members of the group or field. Therefore, once establishing the existence of clay material in a soil sample it is still necessary to determine and evaluate the individual type clay mineral.

Several methods exist by which clay minerals are identified. These are:- the petrographic method, x-ray diffraction, chemical analysis, and of course, differential thermal analysis. The petrographic method is satisfactory when using larger grain sizes

Chemical analysis gives an accurate result, but the method is time consuming, expensive and the manner in which constituents are combined is not indicated. X-ray diffraction and differential thermal analysis, used separately or together, appear to be the more popular identification methods.

Le Chatelier, in 1887, in an investigation of the clay components, was the first person to develop apparatus to measure thermal reactions and to use such data as an analytical criteria for basis of study. Thermal data on halloysite, allophane, kaolin, pyrophyllite and montmorillonite were published as results of this study. Le Chatelier used a single platinum - platinum plus 10 percent - rhodium thermocouple for his work. In 1904, together with Salodin, Le Chatelier presented a paper describing a modified apparatus but in these investigations he was unable to obtain reproducible results.

Until about 1910 the general practice employed a small platinum crucible in which the material was placed. Into the center of the material a single thermocouple bead was inserted. A furnace heated the assembly rapidly, though fairly uniformly, through ranges of temperature comparable to those that are used today. Readings were made by the investigator from a galvanometer connected to the thermocouple leads. Readings were also made by suitable photographic equipment. Reactions in the test material were indicated by differences in the galvanometer readings as compared with those readings made when the furnace

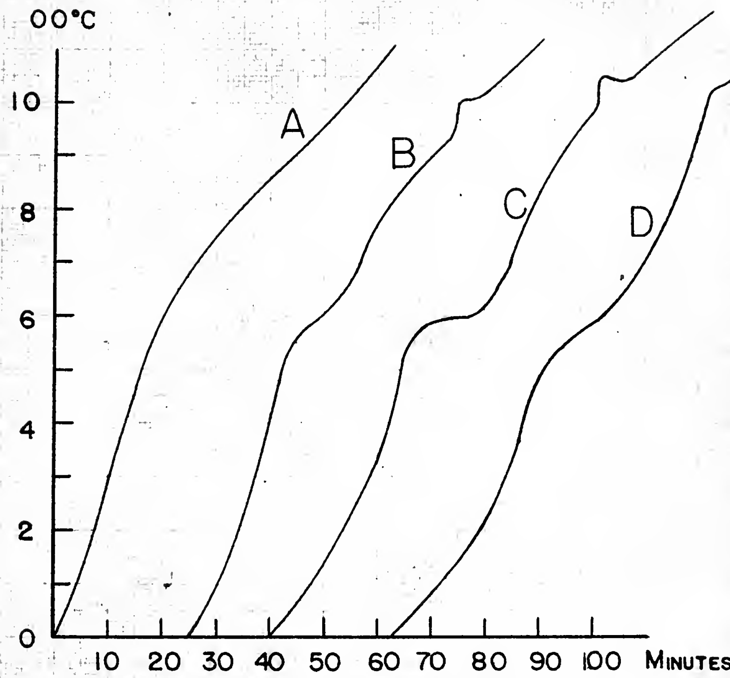
contained no sample. A typical curve would indicate the thermal reactions of the test material superimposed on the heating curve of the furnace. An example, as taken from Grim (6), and originally obtained by Wohlin in 1913 is shown as Figure I.

A notable advance in the field of differential thermal analysis resulted in the development by Roberts-Austen of the differential thermocouple method. In 1899, his method enabled the measurement of differential temperatures between the test material and an inactive material. Burgess, in 1908, amplified previous work and suggested simple, more practicable differential thermocouple circuits. The differential thermal technique has since been used widely by scientists, especially in England, France, Japan and the United States in the field of metallurgy, ceramics, agronomy, geology and engineering.

Fenner, Wallach, and Wohlin each separately studied clays in the year 1913 and presented representative clay curves. Kracek, in 1929, and others studied the high temperature phase changes of clay minerals.

Added stimulus has been supplied in recent years with the availability of automatic recording and temperature control equipment which has provided investigators with reproducible curves and semi-quantitative information. Too, x-ray diffraction methods have aided immeasurably, both in their own right and in combination with differential thermal techniques.

In 1933 and 1935 reports by Orcel and Orcel and Caillere marked the beginning of present day intensified study of the method.



THERMAL REACTIONS SUPERIMPOSED ON FURNACE HEATING RATE.

A FURNACE HEATING CURVE

B TO D CLAYS SUPERIMPOSED ON FURNACE HEATING RATE

FIGURE 1

In the United States, Insley and Ewell (1935) initiated new and improved equipment, employing automatic recording apparatus. Investigators have been numerous in the past twenty years and excellent papers have been presented on many and diverse studies involving the differential thermal technique.

Orcel is generally credited with the suggestion of possible quantitative application of differential thermal analysis, when he presented curves for many of the clay minerals and natural clays. However, it was not until 1939 when Norton (20) presented his paper that a method of quantitative analysis was applied. Norton found that the height of recorded thermal peaks varied with the amount of clay material being tested. His method involves measurement of the area under these peaks and relating it to the area produced when the total sample was of that single material. Norton's results compared favorably with chemical analysis but leaves much to be desired when mixtures are analyzed. Overlapping peaks present an obvious and not easily solved problem.

Many other papers have been presented which deal with a group of clays or a clay mineral in particular and a few of these are cited later in this paper under "Theory".

The differential thermal procedure as practiced today consists of continuously heating a test sample and a thermally inert substance to elevated temperatures and by suitable apparatus measuring any differences in temperature between the sample and the inert substance. The inert substance undergoes no thermal reaction, therefore, the difference in temperature between the inert substance and the sample is then a measure of the thermal reactions taking

place in the test sample. Recorded results are portrayed as a curve in which the abscissa is the sample temperature and the ordinate is the difference in temperature between the sample under test and the thermally inert reference. This curve is sometimes known as a thermogram. Analysis of an unknown consists of comparing the new curve with curves of known minerals.

Costello (4) presented the first paper on differential thermal analysis at Rensselaer Polytechnic Institute in 1948. Equipment used by Costello included a tube furnace for heating the samples, a portable potentiometer to measure induced electromotive forces, and a manually operated variable transformer to control the heating rate.

The Speedomax autographic recorder for recording the samples and differential temperatures was added in 1949. Studies completed using this equipment were presented by Bystrowski (3). Also in 1949, Assistant Professor J. E. Munzer added a Brown Potentiometer to record the standard temperature and to automatically control the heating rate.

The work of Hoskins and Hudson (11) in 1950 first employed the equipment as presently installed. Subsequent work by Merritt and White (18) in 1951 and Harper and Kitterman (10) in 1953 investigated the effects of variable factors on the differential thermal curves of certain clay minerals.

In the thesis presented by Miller (19) in 1954 it was suggested that should differential thermal analysis be conducted in a vacuum chamber an elimination of the thermal effects of organic material present in clay minerals would result. After considerable

delay in delivery of needed equipment, new special combustion tubes considered suitable for employment of the vacuum technique were assembled and tests were conducted to establish the differential curves of certain natural clay samples under vacuum. Miller cited lack of sufficient time to compile to his satisfaction the data necessary to fully illustrate the value of the vacuum technique. Further investigations were recommended to determine the merit of the vacuum technique in its application to clay samples containing organic matter.

B. Statement of the Problem

The problem concerned an investigation of the vacuum technique in differential thermal analysis when applied to samples of natural clay samples which contained known amounts of organic matter. Further, an alternate solution to the vacuum technique was investigated through the use of inert gasses as the controlled atmosphere in which differential thermal analysis was conducted. The implementation of inert gasses, likewise, is discussed through the succeeding sections of this paper.

The presence of organic material in a natural soil sample makes the identification of the clay mineral(s) contained therein a tedious and not entirely satisfactory process at the best. The accepted practice of sample preparation of a clay material suspected of containing organic matter includes chemical treatment of the unknown sample for the removal of the organic materials. It is desired to remove the organic material in order to eliminate the reactions it will undergo when ultimately tested by some

method of identification. These organic reactions in differential thermal analysis tend to mask or eliminate altogether some of the identifying reactions of clay minerals present in the test sample.

Several methods of chemical treatment are utilized for the removal of carbonaceous matter from a natural soil sample. One method involves placing the finely divided soil sample in a solution of hydrogen peroxide followed by treatment of the solid matter with hydrochloric acid. Washing with distilled water several times removes the carbonaceous material. This method of removing organic matter has been cited by Baver. (1) Other methods may employ different agents but the process is essentially identical. That is, carbonaceous matter is chemically treated to form carbonates which are removed through washing and centrifuging. Careful application of this procedure does not entirely remove the organic material present and secondly leaves the investigator with a hydrogen-saturated clay fraction of the sample which need not necessarily be the original form of the clay mineral.

To run an untreated clay sample containing organic material in differential thermal analysis results in the burning of the carbonaceous matter which makes its appearance as an exothermic reaction plotted on the thermogram. This reaction, depending on its magnitude and extent could and does interfere with reactions characteristic of the active clay minerals which might be present. If a method were devised whereby the oxidation of the carbonaceous material was prevented during a test run, such procedure would eliminate the detrimental effects of the carbonaceous reactions and would allow the thermal reactions of the clay fraction

to be plotted without interference.

The objective of the vacuum and inert gasses techniques is the elimination of the oxygen of the air from the combustion tube and consequently the prevention of oxidation of the carbonaceous material. This method of approach would not change the ion saturation of the clay mineral and its effect upon the reactions associated with organic material under testing would have to be determined.

A study of the controlled atmospheres of vacuum and inert gasses with relation to its effects upon chemically untreated clay samples containing organic material was initiated for investigation by this author.

PART II

THEORY

A. General

Thermal properties of minerals have been studied by two methods, equilibrium dehydration and differential thermal analysis. The basis for study by means of the equilibrium method is to measure the loss of weight of a sample material as the material is heated continuously at a constantly rising heat rate. A plot of the percent loss by weight against the temperature gives characteristic curves for clay minerals. In natural clays, the loss in weight which is measured may not be from water loss alone but may be due to the loss of CO_2 from carbonates and to the loss of volatile materials which may be present as nonclay-mineral components. Inherent difficulties of this method which requires weighing of the hot sample and necessitates a constant humidity in the furnace chamber gives strength to the belief that differential thermal analysis is the better method for study of the clay mineral structure. However, the use of equilibrium dehydration to supplement the differential thermal method has proven a valuable adjunct in analyzing the results of thermal reactions of clay minerals.

As stated previously, differential thermal analysis simply consists of comparing the thermal properties of a test material against those of a thermally inactive one such as calcined aluminum oxide (α - Al_2O_3) when the two materials are heated continuously at a uniform rate to higher ranges of temperatures. The two materials are placed separately into recesses of a sample holder and, by suitable apparatus, temperatures of each substance are recorded

as measured by standard thermocouples. A differential thermocouple measures the intensities of the temperature difference between the two materials and this likewise is plotted by suitable automatic apparatus.

Deflections of the thermal curve or thermogram, in an upward direction are endothermic reactions, those in a downward direction are exothermic reactions. Endothermic reactions in clay minerals are attributed to dehydration and to loss of crystal structure in which the sample absorbs heat energy from its surroundings. Exothermic reactions are due to formation of new phases at elevated temperatures and involves an evolution of heat by the specimen.

A basic interpretation of the thermal reactions and their subsequent plot as the thermal curve was originally produced by Spiel (23) in 1945, followed by Kerr, Kulp and Hamilton (14) in 1949. A synopsis of the above cited work follows.

Figure II shows a typical equilibrium dehydration curve and a differential thermal curve for kaolinite. The endothermic reaction is portrayed as an upward deflection and the exothermic reaction is portrayed as a downward deflection from a horizontal base line.

Most investigators conventionally plot exothermic and endothermic reactions in the opposite directions, however, practice at Rensselaer Polytechnic Institute has been to plot these curves as indicated. The curve is a plot of temperature difference (usually expressed in terms of millivolt equivalents) versus sample temperature.

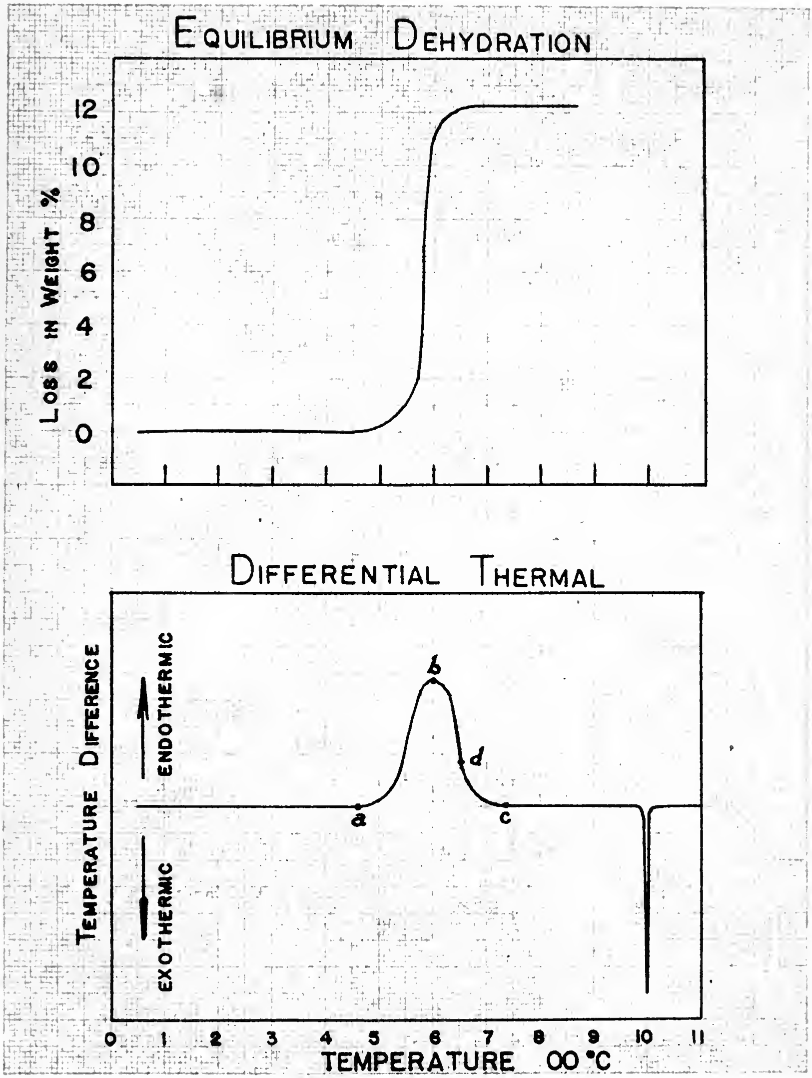

EQUILIBRIUM DEHYDRATION
LOSS IN WEIGHT %
12
10
8
6
4
2
0
DIFFERENTIAL THERMAL
TEMPERATURE DIFFERENCE
ENDOTHERMIC
EXOTHERMIC
b
d
a
c
0
1
2
3
4
5
6
7
8
9
10
11
TEMPERATURE 00 °C

FIGURE II

The endothermic reaction (see Figure II) between 500° and 700° C corresponds quite obviously to the dehydration of the mineral, as seen when compared to the equilibrium dehydration curve. During the endothermic reaction, the test sample absorbs more heat than the inert standard in order to impart energy to the escaping water vapor, which causes the temperature of the test sample and its thermocouple junction to lag behind that of the standard. This temperature difference induces an electrical potential in the differential thermocouple which causes a displacement of the differential temperature plot in the positive (up) direction.

To the left of the temperature at point "a" in Figure II there is no temperature difference recorded between the standard and the test sample. Therefore, the plot of this portion of the curve is a horizontal straight line which represents no lag or lead of the test sample with reference to the inert standard. Heat inflow to both thermocouples of the differential thermocouple is the same. Kerr et.al., state that: "this straight 'base line' is displaced up or down in small amounts according to (1) the relative thermal conductivity of the specimen and the inert sample and (2) the specific heat of the two. Ordinarily, this constant displacement is of no consequence since it does not affect the general shape of the curve".

At "a", in Figure II, the dehydration reaction in the test sample requires an absorption of heat from its surroundings in order to supply the energy for the water vapor escape. The sample thermocouple provides a portion of the required heat energy and con-

sequently becomes cooler than the thermocouple in the inert standard. The induced electromotive force produced in the differential thermocouple during the reaction displaces the plot in an upward (positive) direction until reaching point "b" where the rate of heat absorption by the dehydration of the test sample equals the rate of heat conductivity into the specimen. Between the points "b" and "c" the rate of heat inflow from the block is greater than the rate of heat absorption of the sample. The reaction ceases at a point "d" between points "b" and "c". The location of this point is not known, therefore, it is generally considered that the limits of the reaction are points "a" and "c". At point "c" the temperature of the sample and the inert are again the same. The curve "a - b - c" need not be symmetrical as pictured here. The shape of the curve depends on the nature of the change. For instance, a steep back slope would be characteristic if the mass of the specimen decreases during the reaction as would be the case when decomposition occurs.

In the higher ranges of temperatures the decomposition reaction of kaolinite appears as an abrupt downward reaction of short duration but of large magnitude. Reactions which plot downward from the base line are exothermic in nature during which time heat is liberated from the active material causing the temperature of the thermocouple located therein to be higher than the thermocouple in the inert standard. Therefore, the direction of the induced electromotive force in the

differential thermocouple circuit is opposite to the endothermic reaction and the recorder automatically plots the reaction in the negative direction.

The foregoing should prove of help to the reader in the interpretation of experimental results presented later in this paper.

B. Analysis of Thermal Curves for Natural Samples

Representative natural clay samples were used in these investigations, namely, kaolinite, a montmorillonite (bentonite) and an illite. The thermal reactions of these type clays have been related to the structural arrangement of the crystal lattice by various authors. Explanations of the thermal reactions related to structure have been as numerous as the authors investigating the subject. This has been particularly true of montmorillonite. It is considered altogether proper that the relation of thermal reactions to structures be presented in this paper under this section and, therefore, a correlation of some of the more popular hypotheses regarding this subject are summarized hereinafter.

Kaolin Group:

The kaolin family consists of several members, a few of which are dickite, nacrite, halloysite and kaolinite. These minerals all have certain basic structural similarities, notably the 1:1 crystal lattice. As shown in figure III, the fundamental structural unit appears as a double sheet composed of one gibbsite layer and one silicon-oxygen layer (thus the "1:1" crystal lattice). The gibbsite layer has aluminum in the octahedral coordination, whereas the silicon-oxygen layer has a silicon

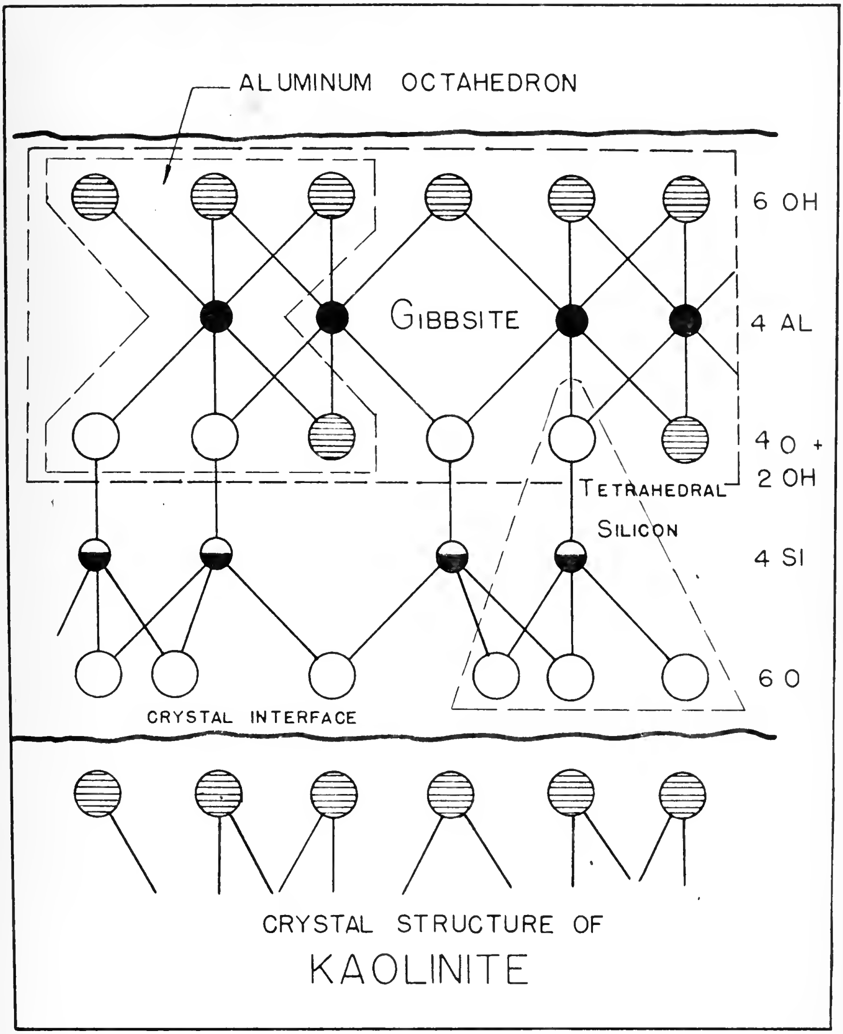
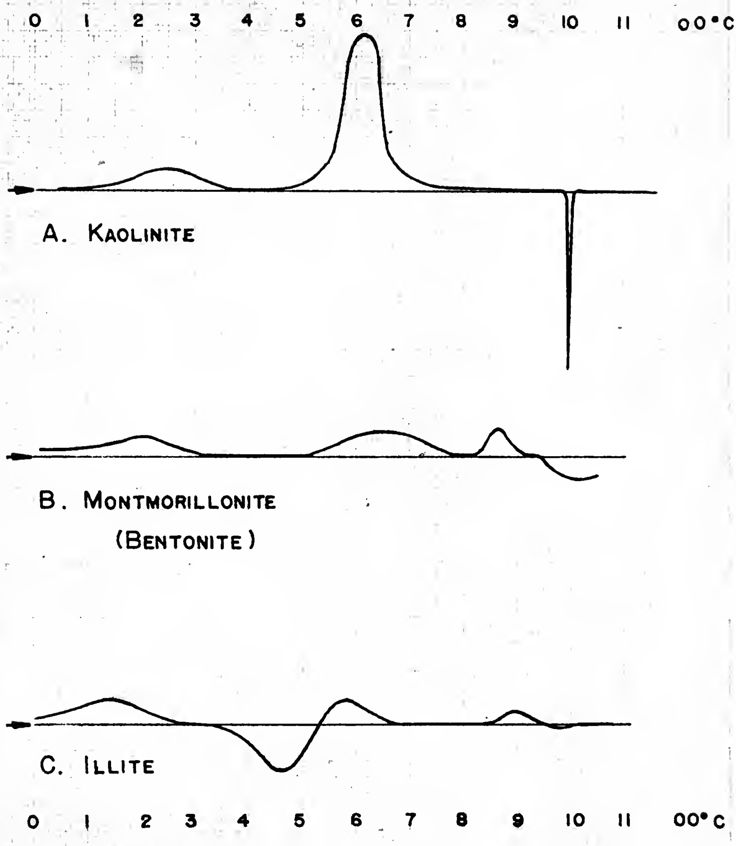

ALUMINUM OCTAHEDRON
GIBBSITE
6 OH
4 AL
4 O +
2 OH
TETRAHEDRAL
SILICON
4 SI
6 O
CRYSTAL INTERFACE
CRYSTAL STRUCTURE OF
KAOLINITE

FIGURE III

tetrahedron. In most mineral forms of the kaolinite family, water is not adsorbed between the sheets since there is a relatively strong bonding action in the attraction of outside oxygen atoms of one sheet to outside hydroxyl molecules of the adjacent sheet. However, halloysite and some forms of poorly - crystallized kaolinite do absorb water between the sheets.

Generally, the thermal reactions of the kaolin minerals may be related to the structural features. Insley and Ewell (12) first attempted to characterize the thermal reactions with known structural concepts. Many other papers followed which described the variations among members of the kaolin group. A typical thermal curve of kaolinite is illustrated as curve A in Figure IV. The kaolin group exhibits only one thermal reaction below 500°C and this is an endothermic reaction at approximately 150°C. Dickite, nacrite and forms of well-crystallized kaolinite do not show this reaction since their structural sheets are perfectly and closely enough stacked so that water molecules do not conveniently fit between the sheets. A small amount of water is absorbed on the edges and corners of the kaolinite structural sheets but not in sufficient quantity to produce an effect on the thermal curve. Any irregularities in the thermal curves in the range of 100°-200°C for these clays are generally attributed to impurities contained in the clay sample.

A major endothermic peak for the kaolin group occurs between 600°and 700°C. The variation in shape of this curve and its position assists in identifying the various members of the group. Kaolinite gives a generally symmetrical curve with a peak at about



Typical Thermal Curves

FIGURE IV

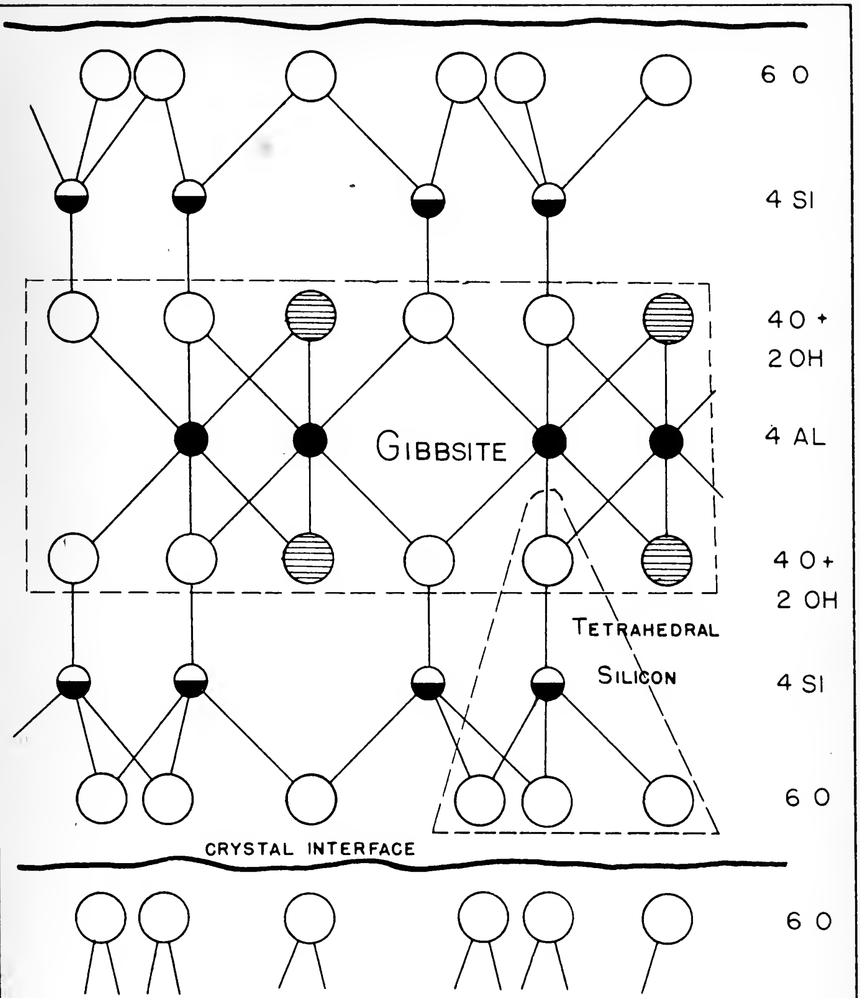
610°C. The endothermic reaction of the kaolinite is attributed to the loss of crystalline OH water and the formation of new amorphous alumina. Grim and Bradley (8) indicate that many forms of kaolinite, in the poorly crystallized varieties undergo complete destruction of the lattice during this endothermic reaction.

All kaolin minerals exhibit a characteristically sharp exothermic peak at 980°-1000°C which is generally associated with the recrystallization of the amorphous alumina to form a gamma-aluminum oxide. Insley and Ewell (12) attribute a strong SiO_2 network to the rather late recrystallization of the amorphous alumina.

Montmorillonite (Bentonite):

The montmorillonite family structure is made up of two silicon-oxygen layers and one gibbsite layer which form a 2:1 lattice structure. The thermal changes which occur upon heating through the usual temperature range of a thermal analysis may be explained in terms of this structure. A montmorillonite crystal lattice is shown in figure V. Variations in the atoms making up the basic crystal units account for differences in the members of the montmorillonite family, i.e., bentonite, pyrophyllite, beidellite and nontronite to mention a few. However, the basic crystalline shape remains the same through all members of the group.

Water molecules are easily absorbed between sheets or structural layers of this type clay. Bonding strength between successive sheets is minimized due to the opposition of like atoms, (oxygen atoms opposing oxygen atoms). Absorbed interlayer



CRYSTAL STRUCTURE OF

MONTMORILLONITE

FIGURE V

ions determine to a great degree the amount of interlayer water which is held within the montmorillonite structure. The space available for water to be absorbed is dependent upon the size and bonding strength of the absorbed interlayer ions. A typical thermal curve for bentonite is shown as Curve B in Figure IV.

The thermal peaks of the montmorillonite family indicate an endothermic peak or peaks between 100° - 250°C. The absorbed water existing between the clay sheets is driven off at these temperatures.

The endothermic peak in the 600°-650°C range is generally attributable to the loss of water absorbed within the layer of the crystal lattice. Some authors indicate that this may be due to the loss of the hydroxyl groups of the crystalline structure expelled as water vapor and, therefore, a destruction of the montmorillonite lattice would begin at these temperatures.

The third endothermic peak occurring in the 850°-900°C range is more often associated with the loss of hydroxyl groups, per Page (21). Others, notably Grim and Rowland (9), indicate this peak is due to lattice rearrangement.

The exothermic reaction at approximately 1000°-1020°C is associated with the formation of spinel. Brindley (2) indicates the final arrangement of montmorillonite to be a crystalline SiO_2.

Illite:

Illites are similar to montmorillonites in structural arrangement, both possessing a 2:1 lattice structure. The absorbed interlayer ion in illites is the potassium ion and its presence produces a strong bonding attraction between the layers of the illite sheets. The potassium ion is extremely difficult to dis-

place and likewise, prohibits the absorption of water between the layers. A curve of the Morris, Illinois illite is shown as an example in Figure IV curve C.

As in the case of montmorillonites, the first endothermic peak indicates the loss of absorbed water between the sheets. The second endothermic peak is attributable to the loss of hydroxyl (OH) water per Grim and Bradley. They indicate the resulting mineral is essentially micaceous but anhydrous. The final endothermic peak which occurs in the range of temperatures of 850°-950° C represents the final destruction of the illite lattice. Thereafter, spinel crystallizes and grows up to 1100°C which gives the small exothermic peak sometimes noticed immediately after the third endothermic peak.

In the illite sample supplied for use in these experiments, a certain amount of organic matter is known to be present. An exothermic reaction, the peak of which occurs at 460°C is attributable to the organic material and may be noticed as the large downward deflection of curve C in Figure IV.

PART III

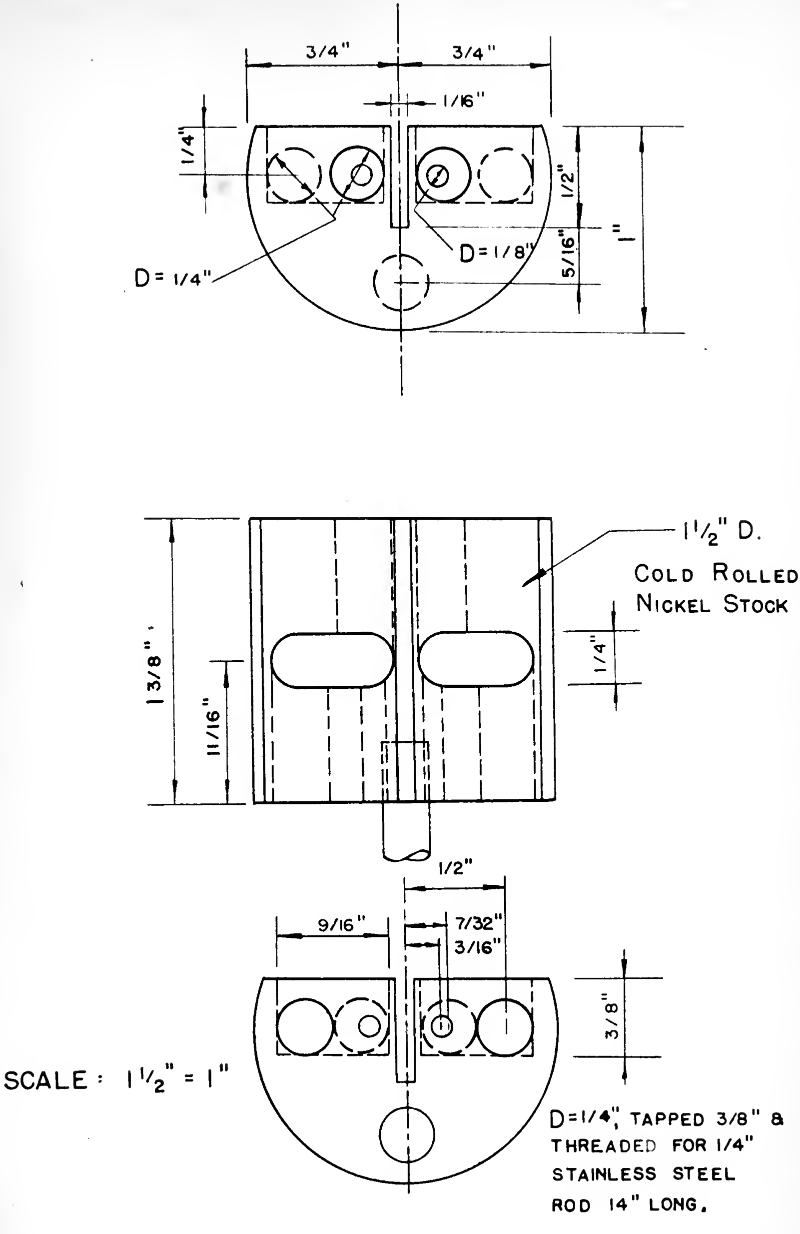
APPARATUS AND MATERIALS

A. General

The apparatus available at Rensselaer Polytechnic Institute for differential thermal analysis is, in general, standard equipment for laboratory experimentation in this field. A comparatively few minor changes in the equipment used by previous investigators at Rensselaer have been made in order to study differential thermal analysis when conducted under vacuum and when conducted in an atmosphere of inert gas. The apparatus and materials used in these investigations are described in the following paragraphs. Modifications cited above are likewise contained in the detailed description of component parts of equipment to follow.

B. Sample Holders

Sample holders used in these investigations were designed by Professor J. E. Munzer of the Civil Engineering Department of Rensselaer Polytechnic Institute. The sample holder is a machined block of $1\frac{1}{2}$ inches diameter cold rolled nickle stock, 1 3/8 inches long and an inch in depth. A detailed drawing of the sample holder is shown in Figure VI. The holder contains two sample wells, each of which is $\frac{1}{4}$ inch by 9/16 inch and 3/8 inch deep. Into one well is placed the sample to be tested and into the other well is placed the thermal standard. A slot 1/16 inch wide and 1/2 inch deep separates the two wells in order to reduce heat transfer between them. Through holes machined into the ends of the holder, two thermocouples are inserted into each well. One thermocouple is a



SAMPLE HOLDER

FIGURE VI

conventional temperature measuring thermocouple and the other is a differential temperature thermocouple which is used to connect the two wells. The sample holder has been mounted on a $\frac{1}{4}$ inch stainless steel rod to facilitate placing and removing the holder from the furnace. The rod serves conveniently as a brace to which are securely bound the porcelain tube insulators through which the thermocouple leads are brought to the holder.

C. Thermocouples

All thermocouples were made from Brown and Sharp 18 gage chromel and alumel wire stock. Two methods were used to fuse thermocouples used in this study. Initially, thermocouples were fused by use of a direct current carbon arc using borax as a flux. Equipment used is located in the Metallurgy Department, Room 404, Ricketts Bldg. This method requires some degree of experience to make thermocouple beads small enough for satisfactory use in differential thermal analysis. At one time during these studies it was surmised that this method of manufacture could be the cause for breakage during test runs of the thermocouples and their leads. Thermocouple breakage is discussed in detail under "**Results and Discussions**". Therefore, all subsequent thermocouples were fused by use of an electric arc as had originally been done by Harper and Kitterman, (10). The method is considered of sufficient merit to describe in some detail here.

Fusion of the thermocouple wires is accomplished in the electric arc method when a spark is induced by near contact of the thermocouple wires and a layer of mercury contained in a

50 milliliter pyrex beaker. The thermocouple wires and the layer of mercury (approximately $\frac{1}{2}$ inch in depth) are, in effect, made the "hot leads" of a broken electrical circuit. Thermocouple wires are clamped to one circuit lead, and through a copper strip terminating within the layer of mercury, the mercury is made the other lead of the broken circuit. When the thermocouple wires are brought close to the surface of the mercury, a spark of such heat intensity as is required to melt the thermocouple leads is produced and fusion results. Heat produced by the electrical spark and the heat of the fused thermocouple bead is quenched in a thick layer of oil which rests atop the mercury and fills the beaker. A 125 volt, D. C. current source was provided and 8 to 10 ohms resistance was supplied by a sliding wire type resistor manufactured by Central Scientific Co., Chicago, Ill. The variable control of the resistor is set by trial and error methods to give desired magnitude of spark to fuse thermocouple leads. As indicated above, the author determined 8 to 10 ohms resistance was adequate for the type and gage thickness of thermocouple wire welded. A schematic diagram of this equipment is provided in Figure VII. This apparatus is also maintained by the Metallurgy Department on the second floor of the Blaw Knox I Building.

Thermocouples fused by the electric arc method offer several advantages. Smaller, more satisfactory beads were produced at the joint by this method than by the carbon arc method. Moreover, thermocouples made by the electric arc method were made more easily and in considerably less time. Little previous

Electric Arc Circuit

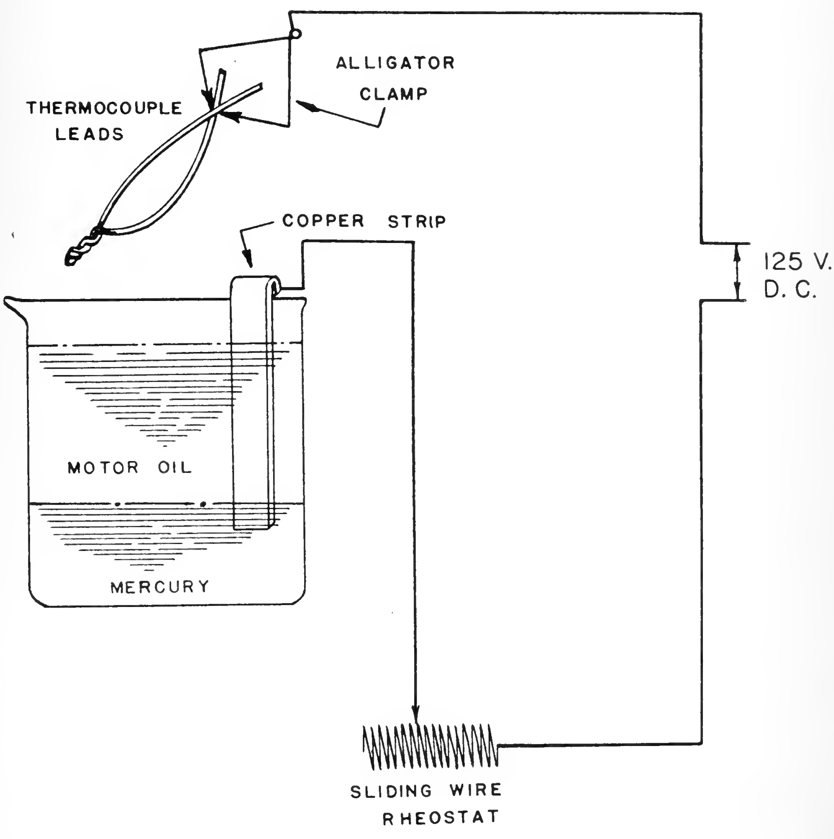


FIGURE VII

experience is required to make satisfactory thermocouples by the electric arc method.

The differential thermocouple consists of two leads of chromel wire connected by thermocouples to a short length of alumel wire Thermocouple junctions are centered in the sample wells and are held in place by porcelain tube insulators which carry the thermocouple leads outside the furnace. The leads are merely soldered to the prongs of an octagonal male plug. This plug connects to its female counterpart which is secured to the bench supporting the furnaces and is connected to the recording equipment.

D. Thermocouple Tester

A convenient and useful addition to the equipment to be used with the differential thermal analysis apparatus is the thermocouple tester developed by Harper and Kitterman (10). During these investigations, frequent breakage of thermocouples occurred. The testing apparatus provided a most expedient and reliable method to determine the electrical continuity of thermocouple circuits before and after each test run.

The tester simply consists of a D.C. ammeter which is connected successively through a multiple position switch to each of the three thermocouples in the sample holder. A common 1.5 volt flashlight battery provides the necessary electrical current.

E. Furnaces

Three electric test furnaces are provided. They are horizontal, heavy duty, combustion type, Hoskins Model FH-305, 12 inches long with an inside diameter of 2 1/32 inches. All furnaces contain

1750 watt heating elements which are supplied through a two-kilowatt transformer, the maximum output of which is 17 volts and 118 amperes. The transformer supplies, as required, each furnace through its individual single-throw knife switch. Knife switches are mounted on a panel beneath the furnace bench. A $1\frac{1}{2}$ inch. I.D. alumina combustion tube, 12 inches in length is normally used in the standard test runs of differential thermal analysis under atmospheric pressure.

Furnace No. 1 was used throughout the experiments to make tests under atmospheric pressure and, therefore, exclusively employed the 12-inch cemented alumina combustion tube.

During the preliminary stage of the investigations, a 12-inch combustion tube made of fused silica (fused quartz) having a sand surface finish was used in Furnace No. 2. Test runs were conducted under atmospheric conditions while the 12-inch tube was employed. As the investigations progressed, the 12-inch combustion tube was replaced by a 24-inch tube of the same material and finish to be used as an enclosure for an atmosphere of inert gas in which the differential thermal analysis was to be studied. The tube was procured with one end closed and the interior of the open end finely polished and rounded, suitable for insertion of rubber stoppers.

Furnace No. 3 was similarly outfitted for investigations under vacuum. The combustion tubes of fused silica were purchased from the Thermal American Fused Quartz Co. of Lynbrook, New York under the trade name of "Vitreosil".

F. Recording Equipment

The temperature of the test sample and the differential temperatures are recorded by a Type G, Model S-60000 Series, Speedomax, manufactured by the Leeds and Northrop Co. The range of temperatures which may be recorded by the Speedomax is from 0 to 1200 degrees Centigrade. Differential temperatures can be recorded from plus to minus 1.5 millivolt equivalents. When this recording apparatus is operated as a two-point recorder, the thermal curves are plotted directly on paper calibrated in degrees Centigrade with successive points being plotted every six seconds. The temperature of the test sample, therefore, may be read directly from the recording paper; however, in order to properly evaluate the differential temperature curve it is required to scale values of millivolt equivalents from the thermal curves.

To continuously record the temperature of the standard sample, a Brown Recording Potentiometer Pyrometer, Model No. 113661-X54#1-H was used. The recording instrument has a temperature range of 0 to 1400 degrees Centigrade and is used to control the rate of increase in furnace temperature as described below.

G. Temperature Control

A constant rate of temperature rise within the furnace is attained in the following manner. A "temperature control indicator" moves across the face of the Brown Potentiometer at a constant speed which is established by a ratio of gears in a

chain drive mechanism. This indicator merely indicates the desired constant rate of temperature rise in the furnace. Likewise, moving across the face of the Potentiometer concurrently with the "temperature control indicator" is the "furnace temperature indicator" which registers the temperature of the standard sample in the sample holder. When the "furnace temperature indicator" lags or leads the "temperature control indicator", a compensating adjustment is made in the position of a motor-driven variable transformer, Variac V-20. The Variac thereby controls the voltage input to the primary of the furnace transformer. Thus, a displacement of one indicator from the other serves to continuously adjust the voltage placed across the furnace in order to maintain a constant temperature rise in the furnace. The Variac has a rated output of 3.45 kilowatts and operates between 0 and 135 volts.

A compensating rheostat is provided in the control circuit which must be properly set to supply the correct initial voltage from the Variac to the furnace so that a uniform rise of furnace temperature results. Improper setting of the compensating rheostat will cause the temperature control mechanism to "hunt", that is, first a slow rate of temperature rise develops, followed by too fast a rate and so on. A fluctuating heating rate is neither desirable or satisfactory for usable data.

H. Vacuum Equipment

The vacuum in these investigations was maintained through use of a CENCO Pressurevac-4, pressure-vacuum pump manufactured by the Central Scientific Co., Chicago, Ill. By continuous operation of the vacuum pump, a pressure of .5-.6 mm of absolute pressure could be maintained in the combustion tube. A McLeod gage, manufactured by the Scientific Glass Apparatus Co., Inc. of Bloomfield, N. J., accurate to .01 mm of mercury absolute pressure, was used as a vacuum measuring gage.

The assembled sample holders which were used under vacuum were of a somewhat different make up than those used under standard atmospheric conditions. Porcelain tube insulators were extended the length of the thermocouple leads which remain inside the special 24-inch combustion tube during test runs. In assembly, the thermocouple leads were inserted through a No. 9 rubber stopper which provides the seal for the open end of the combustion tube. In addition to the six thermocouple leads, the stopper was punched to accommodate the insertion of a $\frac{1}{4}$ inch glass tube. Connection from the vacuum pump to the glass tube was made by vacuum rubber tubing. All connectors in the system were metal "tees". "Bear-cat" Weatherstrip Adhesive, manufactured by Behr-Manning, Troy, N. Y., was used as a sealing compound where thermocouple leads and glass tubing make contact with the rubber stopper on its outside face.

I. Inert Gasses Equipment

Commercial cylinders of inert gasses were used as the source of a fixed atmosphere. Helium and nitrogen were used in these investigations as representative inert gasses. Necessary

pressure reduction valves were borrowed from the Metallurgy Department.

Assembly of the mounted sample holders was similar to that used in vacuum tests in that thermocouple leads passed through a No. 9 rubber stopper together with glass tubing. In this instance, two lengths of glass tubing were required to pass into the combustion tube through the rubber stopper, one for inflow of the inert gasses, the other for exhaust. The length of inflow tubing extended beyond the rubber stopper some 12 inches into the combustion tube. Thereby circulation of inflow gasses throughout the combustion tube was insured before they were exhausted at the stoppered end of the tube. Exhaust gasses were conducted by glass tube from the combustion tube to a suction flask where they were allowed to escape under water bath. Continuous flow of the inert gas through the combustion tube was maintained by adjusting the pressure regulating valves to allow a slow escape of exhaust gasses which were observed visually as bubbles escaping beneath the surface of the water in the suction flask.

J. Preparation Apparatus

Test samples were preheated in an Elconap Oven, Model DPC-M-60292, manufactured by the Electric Heat Control Apparatus Co., Newark, N. J. A Hevi-Duty Multiple Unit Electric Muffle Furnace, Type 66-P, manufactured by the Hevi-Duty Electric Company, Milwaukee, Wisconsin was used for thermocouple calibrations. A Cenco-Meinzer Sieve Shaker, Cat. No. 18480 was employed to sieve test materials.

K. Clay Mineral Samples

These standard clay minerals were used in these tests: H-9 Kaolinite, Mesa Alta, New Mexico; Montmorillonite, H-24 Bentonite,

Otay, California; and H-36 Illite, Morris, Illinois. The clay minerals were obtained from Ward's Natural Science Establishment, Inc., Rochester, N. Y.

Two unidentified field samples were provided by Professor Kilcawley of the Civil Engineering Department. These two soil samples were received from the St. Lawrence Seaway project for identification.

L. Organic Materials

Five laboratory organic materials were used to mix with standard clay samples in these investigations. They are considered representative of such organic matter which may be present as foreign matter in clay samples. The materials described below were mixed with the standard clays to make up test samples which were investigated under the vacuum and inert gas atmospheres

Organic Materials were the following:

a. Activated Carbon: "Aqua Nuchar" produced by West Virginia Pulp and Paper Co.

Analysis: not available

b. Lactose, Powdered: "Bakers Analyzed", J. T. Baker Co. Phillipsburg, N. J.

Analysis:	Wt. %
Non-Volatine material	.02
Dextrine	.00 (trace)
Sucrose	.00 (")
Heavy Metal (like Pb)	.0004
Iron	.0003
Glucose	.05

c. Wood flour: Manufactured by Brown Paper Co.
Berlin, N. H. of soft woods.

Analysis: Not available

d. Alpha-cellulose: Highly purified derivative of wood cellulose, manufactured by Brown Paper Co., Berlin, N. H.

Analysis: Not available

e. Sewage Sludge: Well digested primary sludge, furnished by Sanitary Division of the Civil Engineering Department.

M. Inert Gasses

Inert gasses used in these experiments were nitrogen and helium. These gasses were considered to be representative of those gasses classed as "inert", and as such, results obtained during these investigations are considered to be those obtainable under other gasses of this category. Available descriptive analysis follows:-

a. Helium: Manufactured by Air Reduction Company

Type: Welding grade, double charcoal refined,

Grade XX	Weight %
CO_2	0.0006
A	.0005
H_2	.00003
N_2	.002
CH_2	.000002
O_2	.00 (trace)

b. Nitrogen: Manufactured by: Linde Air Co.

Type: Orange ring, H P dry

Analysis: 99.99% purity

Moisture: 15 grains/1000 cu. ft. maximum

Impurities: Oxygen, less than 100 ppm.

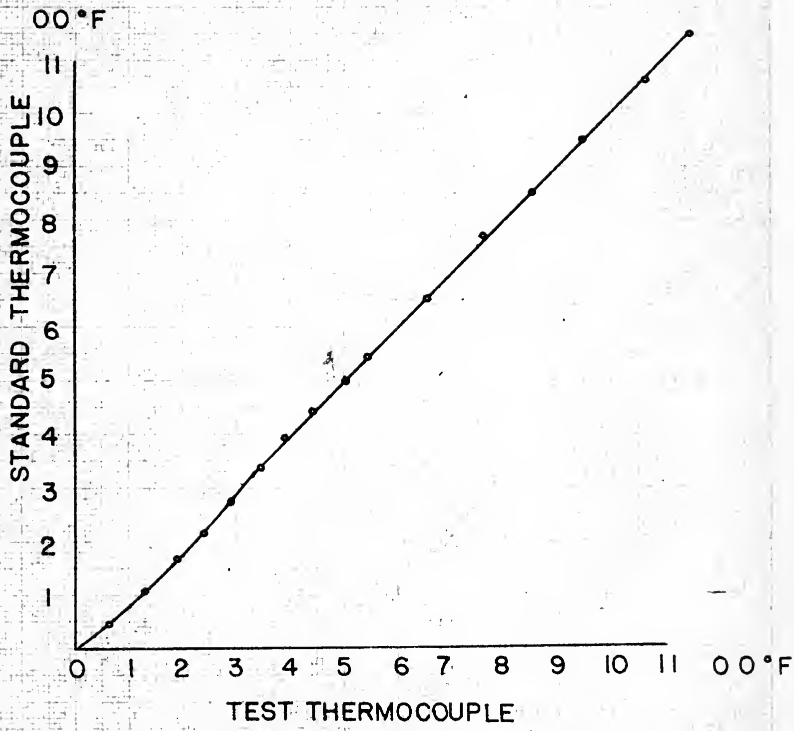
N. Equipment Calibration

1. Temperature Thermocouples

Temperature thermocouples were calibrated against a standard thermocouple by placement in the muffle furnace and heating together through a temperature range of 1100 degrees Fahrenheit. The standard thermocouple had been previously calibrated by Hoskins and Hudson (11). The induced electromotive force of the standard and test thermocouples were measured by a Brown Portable Potentiometer Model 126W3 manufactured by Minneapolis Honeywell Regulator Co. By switching leads of the test thermocouples at the potentiometer terminals during intervals of rise of the furnace temperatures, two thermocouples could be calibrated simultaneously. All thermocouples had slight variations from the standard thermocouple at temperatures below 300°C and corrections were made in values plotted below this temperature. A sample calibration curve is shown in Figure VIII. Thermocouples were lettered for identification purposes when assembled in the sample holders such that proper corrections could be applied to test data for those thermocouples which deviated from the standard.

2. Differential Thermocouples

Calibration of the differential thermocouple was accomplished after the sample holder had been assembled. Equal quantities of



THERMOCOUPLE CALIBRATION CURVE

FIGURE VIII

alumina were placed in both the sample and standard wells and a test run completed in the Hoskins furnace. The plot of the differential temperature curve as recorded by the Speedomax established a base line for that thermocouple under conditions of the particular test run. This calibration was accomplished under each type atmosphere in which the sample holder was placed in service. Faulty differential thermocouples could be easily detected by an irregular base line plot on the Speedomax. A satisfactory differential thermocouple record is characterized by a vertical straight line trace.

3. Recording Equipment

The recording equipment was calibrated during its initial installation by Assistant Professor J. E. Munzer and by Hoskins and Hudson. Prior to use by this author the equipment was rechecked by Professor Munzer for proper operation.

PART IV

PROCEDURE

A. General

The intent of the Procedure section has been determined as being twofold. First, it is considered that particular mention should be made of the procedure adopted for operation of the equipment. This material shall be covered in some detail in the following subsection entitled "Operational Procedure". An attempt will be made to encompass the intricacies of equipment operation with only minimum repetition of material described previously. It is the desire of the author to merely supplement the preceding descriptive sections with amplifying operational details only. Therefore, the reader is invited to make liberal reference to the equipment description subsections of "Apparatus and Materials" if descriptive matter appears inadequate within these sections.

A second subsection included herein is entitled "Method of Procedure" in which a general outline of the approach to the problem is presented. The object of the subsection is to summarize without excessive detail the several phases in which test investigations were divided in logical sequence.

B. Operational Procedure

1. General

It is deemed appropriate to mention at this point the detailed requirements which are considered prerequisite to satisfactory thermal procedure. Lambe (15) has formulated a detailed analysis of those theoretical requirements which must be applied with care in thermal analysis. The problem of obtaining reproducible curves becomes easier with the application of these considerations. Lambe's observations are considered of sufficient importance to be included in original form as follows:

"1. The mass, specific heat and conductivity of the sample must be equal to those of the inert.

These properties depend on the particle size and shape, void ratio (degree of packing), moisture content, and specific gravity of both the sample and the inert. Void ratio and moisture content can be controlled, but little can be done about the other variables. Changes in mass, specific heat and conductivity which occur in either the inert or the sample because of temperature changes, or in the sample because of reactions such as decomposition, can be controlled only slightly.

2. The beads on the differential thermocouples must be located at the centers of the sample and the inert.

Since there are thermal gradients in both the sample and the inert, it is necessary that the couple bead....... be at the same corresponding location, the center being

the most convenient, in order that the temperature drops from the heat transfer be the same.

3. The inert material must be truly inert [thus have no thermal reactions in the range of the investigations].

4. The sample and the inert must reside in an infinite thermal reservoir. [This requirement is attained by the use of a container of sufficiently large mass that its temperature is unchanged by reactions taking place within the test sample.]

5. Symmetry in container. Since there are thermal gradients in the container, the sample and the inert must be located exactly symmetrically in the block in order that they get the same heat from the source of supply.

6. Particle size of the sample......The magnitude of thermal reactions and the temperatures at which they occur can be influenced by specific surface."

It is the author's belief that those items stated above have been complied with at Rensselaer and in these investigations. Procedure adopted in these studies would fulfill those requirements not already complied with in design of equipment. Merritt and White (18) and Harper and Kitterman (10) made investigations relative to the variations of standard clay thermal curves when the variable factors of grain size, heating rate, etc. were considered. Procedures outlined by these investigators generally were used in these investigations.

2. Preparation of Sample

All sample material, clays and organic matter, were of clay particle size; that is, that material passing a 200 mesh sieve.

This size gives adequate surface area as required in the considerations of Lambe above, and enables this author to verify results of the natural clay samples run in previous years on the same equipment.

Experimentation indicated that proper mixture of clay - organic material should be no greater than 10 percent by weight of organic matter as compared to natural clay sample. Satisfactory and representative thermal curves were obtained through use of a clay-organic material mixture of 95 percent clay sample and 5 percent organic additive. "Results and Discussions" treat this problem in more amplifying retrospect.

All test materials were stored in sample bottles placed in a drying oven for at least 24 hours preceding tests. The oven temperature was maintained at 100°C.

In accordance with Lambe's recommendations the inert material, gamma-aluminum oxide (alumina), was preheated to 300°C to remove any adsorbed moisture. When the alumina was newly prepared it was preheated at that time and allowed to remain in the drying oven at 100°C until used in a test run. Lambe indicates that the alumina must be heated to 300°C and allowed to cool in a desicator preceding each run. Harper and Kitterman (10) determined no effect was noticeable if the alumina remained stored indefinitely in a drying oven at 40°C after once heating to 300°C. Therefore, it was assumed that retention of the alumina in a drying oven at 100°C likewise would fulfill satisfactorily requirements for a water-free inert substance.

Test samples and the inert material were weighed to the nearest .0001 gram. In general, samples used in these investigations were .7000 gram. Instances where other sample weights were used are so noted in data presented. In most cases the .7000 gram weight of sample insured proper coverage of the thermocouple beads in the sample wells.

In all cases the sample weight was the same as that of the inert material. In those cases where tests under atmospheric conditions were compared to tests conducted under vacuum or on inert gas all weights of samples were equal.

Materials were compacted in the sample wells by compressing in successive layers. A nail whose head had been filed to fit exactly into the sample well was used as a tamp to compact the sample materials. Gentle pressure applied by hand served to satisfactorily compact the successive layers.

Difficulties were encountered in the degree of compaction necessary when samples were tested under vacuum. Discussion of these problems is treated under "Results and Discussions".

3. Thermocouples

Before and after each test run the thermocouple circuits were tested by use of the thermocouple tester (see"Equipment") to insure that circuits were complete. Per Lambe, each thermocouple head was checked to determine if its location was proper: that is, if not centered in the sample well, each was placed in a corresponding location. Thermocouple leads were inspected to insure that porcelain insulators were in position to keep

leads from touching the sample holder. Bare portions of the leads were inspected to determine that no short circuits existed.

4. Heating Rate

Experimental results obtained by Hoskins and Hudson (11) determined that the best working curves were obtained by the apparatus used at Rensselaer by employing a heating rate of 1023°C per hour. On the basis of these results the heating rate was maintained at this value. This heating rate which approximates 17°C per minute is somewhat higher than the average rate, which is about 12.5°C per minute, used by most investigators.

As discussed in the section entitled "Apparatus and Materials" the heating rate is established through a gear and chain drive arrangement operating from the Brown Potentiometer. A mechanical cut-off switch is tripped and all power input to the equipment is stopped when the temperature control indicator reaches 1200°C. The mechanical cut-off switch may be set to stop the operation of the equipment at a lower temperature. In these investigations the test runs were set for completion at 1050°C, with several runs being allowed to continue to 1100°C. This phase of operations is indicated later in "Results and Discussions".

5. General Test Procedure

A test procedure was adopted which incorporated the recommendations of previous investigators who had used the equipment. The test procedure outlined below was followed in order to maintain uniform test procedures and to attempt to obtain reproducible thermal curves:

1. Several test runs completed initially, established the settings required on the compensating rheostat (as explained under "Apparatus and Materials"). A correct setting is necessary for use with each furnace. Settings used during these investigations were all set within 1/8 inch to the left of the zero mark on the compensating rheostat.

2. All materials were prepared, heated, weighed, and placed in sample holders in accordance with procedure described in subsection 2., "Preparation of Sample".

3. The loaded sample holder was carefully placed within the furnace combustion tube to be utilized for the particular test run.

4. The Brown Recording Potentiometer was turned on, manually balanced, turned off, and the temperature control indicator (black pointer) and the furnace temperature indicator (red pointer) were both set at 75°C.

5. Thermocouple leads from the sample holder were connected to the recording equipment circuits by plugging in the octagonal male plug.

6. Proper connection of circuit leads at the terminal blocks were checked and changed, if necessary, to accommodate the particular sample holder used in the test run.

7. The Speedomax was than placed in operation, and manually balanced.

8. The knife switch to the furnace to be placed in use was closed and the test run started.

9. When the temperature of the test sample reached 75°C, as indicated by the Speedomax, the Brown recorder was placed in operation.

10. When the temperature of the inert standard reached 1050°C the automatic cut-off switch on the Brown Recorder shut-off power to all equipment and the test was completed.

In the test procedure outlined above the setting of the compensating rheostat in step (1), together with steps (4) and (9), virtually eliminated the "hunting" effect of the temperature control mechanism.

6. Vacuum Application

When test runs were conducted under vacuum the special sample holder (refer "Apparatus and Materials") was used. The loaded holder was inserted in a furnace equipped with the special 24-inch fused silica combustion tube and the rubber stopper at the open end of the tube was carefully and firmly inserted. Connection was made from the vacuum pump by a section of vacuum rubber tubing to the glass tube which passed through the rubber stopper and into the furnace chamber.

The vacuum pump was placed in operation and the combustion tube evacuated previous to starting the test run. In these investigations the vacuum was placed in operation between steps (7) and (8) of the procedure outlined in the preceding subsection.

Absolute pressure in the vacuum system was measured at frequent intervals during the test run by use of the McLeod gage. The vacuum maintained by continuous operation of the vacuum pump measured in the range of .5-.6 mm. of absolute

pressure. Continuous pump operation was necessary to maintain constant pressure throughout a test run.

7. Testin Under Inert Gasses

An inert gas was introduced into the combustion tube by means of a glass tube through the rubber stopper similar to that used to evacuate the test chamber in the vacuum technique. See "Materials and Apparatus" section. A second glass tube through the stopper allowed exit of gasses from the combustion tube. Proper adjustment of the pressure regulating values allowed the inert gas to enter the combustion tube at approximately one pound absolute pressure above atmospheric. Steady flow of inert gasses was maintained as explained under "Materials and Apparatus". The flow of the inert gas was properly regulated through the combustion tube prior to starting the test run. In these investigations the flow of inert gasses into the combustion tube was begun as an additional operation between steps (7) and (8) under the subsection 5. "General Test Procedure".

8. Test Data

Certain test data was considered essential over and above the [illegible]hic records produced automatically by the two recorders. [illegible] book was maintained during these investigations in which [illegible] recorded the following specific data for each test run.

a. Number of test. Identifying markings were made on the Brown and Speedomax plotted curves such that correlation of recorded test data could be made with automatically plotted curves.

b. Sample tested. The mineral name, with amount and type of material mixed therein, if any.

c. Weights of Sample and Standard.

d. Date of Test.

e. Type of Atmosphere enclosed. When vacuum used, readings of vacuum gage at intervals.

f. Thermocouple identification. Used to correct recorded curves per original thermocouple calibration curves.

g. Cold Junction Temperature.

h. Remarks. Any pertinent information which may develop during testing, such as deviations from standard practice, malfunctions of equipment, etc.

9. Cooling Furnace

Furneces require from six to ten hours to cool to room temperature after a test run. Therefore, maximum utilization of time cannot be made under these circumstances. Previous investigators have cited methods attempted to increase the cooling rate, however, these methods met with little success. Without the added installation of still another furnace only careful planning and scheduling will enable a maximum of six runs a day. Three test runs performed in the morning with three additional late evening runs were accomplished and considered maximum usage of present equipment.

C. Method of Procedure

The problem has been described heretofore but is repeated at this juncture at the expense of apparent redundancy, but in the interests of adding continuity to this section. The stated problem was to determine the effect of the application of vacuum during thermal analysis when test samples contained known amounts of carbonaceous material mixed therein. The proper manner in which to approach the problem seemed to divide itself quite logically into four parts. Firstly, it appeared necessary to devote some time to becoming acquainted with the apparatus through testing of known clay samples. Therefore, it was decided to run the first series of tests under normal atmospheric conditions on selected natural clay samples alone in order to establish the curves obtained by previous investigators. Further, these tests enabled the author to familiarize himself with the operation of the apparatus and provided ample experience to devise workable operational procedure. Natural clay samples to be used in the later series of tests were employed in these tests of the first series.

A second series of tests appeared to be necessary in order to establish the curves of the natural clay samples under vacuum. Assuming satisfactory results were obtained under the first two series of tests, procedure would allow progress to those tests designed to evaluate the effect that an applied vacuum would have upon carbonaceous material mixed with the standard clay samples. A third series of tests then would consist of establishing

curves for the individual standard clay samples when mixed with the organic material and tested under normal atmosphere. Several organic materials were selected to be mixed individually with the clays, description of which were given under "Apparatus and Materials".

The fourth group of tests, it follows, would be to test these same mixed samples under vacuum to establish the accuracy of the postulation relative to the expected elimination of the thermal reactions of the organic material.

A fifth series of tests were included when during the course of the investigations it was decided to employ the inert gasses as a substitute atmosphere for vacuum. Reasons therefor are discussed in the section of this paper entitled "Results and Discussion". It was anticipated that thermal curves of this group of tests could be compared with those curves obtained in the third series of tests and the effect of inert gasses upon thermal analysis could be illustrated.

The problem of what organic material to be included in the clay samples was resolved in the application of the following material quoted from Grim (6). He states:- "In general, the organic material occurs in clay materials in two ways:- it may be present as discreet particles of wood, leaf-matter, spores, etc. or it may be present as organic molecules adsorbed on the surface of the clay mineral particles. The discreet particles may be present in any size from large chunks easily visible to the naked eye to particles of colloidal size which act as pigment in the clay-mineral material."

Logic dictated that tests should be conducted first on clay samples which would include organic material mixed therein in the form of discreet particles. The "discreet particles" could be conveniently weighed and therefore, known amounts would be tested. Careful mechanical mixing of the clays and organic material would be sufficient to represent the clay minerals containing organic material as found in nature. Finely divided solid particles of laboratory-prepared organic materials were obtained; their preparation was covered in the preceding subsection 'Operational Procedure'.

The above breakdown represents the five phases into which all tests were divided. However, since the furnaces were not outfitted for similar usage, test runs of separate phases were performed concurrently in order to establish maximum use of all furnaces. After the first series of tests had been concluded to satisfaction, the sample holder and combustion tube used in Furnace No. 2 were replaced by holder and tube developed for operation under vacuum. Thereafter, it became expedient to make test runs of series Nos. 2, 3, and 4 concurrently in order to use all available furnaces each operating day. Furnace No. 1 which had not been made suitable for vacuum operation was used as the test furnace in which the third series of tests were conducted. These tests were performed as noted above, on mixtures of natural clay samples and organic materials. Furnaces Nos. 2 and 3 were employed for use in test series Nos. 2 and 4 under vacuum.

PART V

RESULTS AND DISCUSSIONS

A. General

Both results and the discussions thereof shall be considered in this section. To indicate results obtained and the discussions pertaining thereto in separate sections, it seems to the author, would require unnecessary repetition of subject matter and require unnecessary back reference by the reader, not to mention that continuity of thought would be hampered if not destroyed. Therefore, in the interests of better thesis organization, brevity and clearness of thought, the author has included results and discussions under the same title heading.

The general outline of results and discussions to be presented herewith, will follow in general the testing procedure as outlined in the previous section. Data and results observed during the first and fifth phases of testing shall be discussed in separate sections. In view of concurrent testing in phases Nos. 2, 3, and 4, results and discussions of these series of tests are presented as one subsection. Certain correlation between test series necessarily will be required and shall be inserted as deemed proper to support the objectives of the thesis problem.

Some problems encountered and phenomena observed appear to have logical and plausible answers and these are brought out in the discussions. However, as is true in all phases of research, there are those problems to which ready solutions do not seem available. This thesis presents several of the latter type problems and correct solutions necessarily will await subsequent study by investigators to follow.

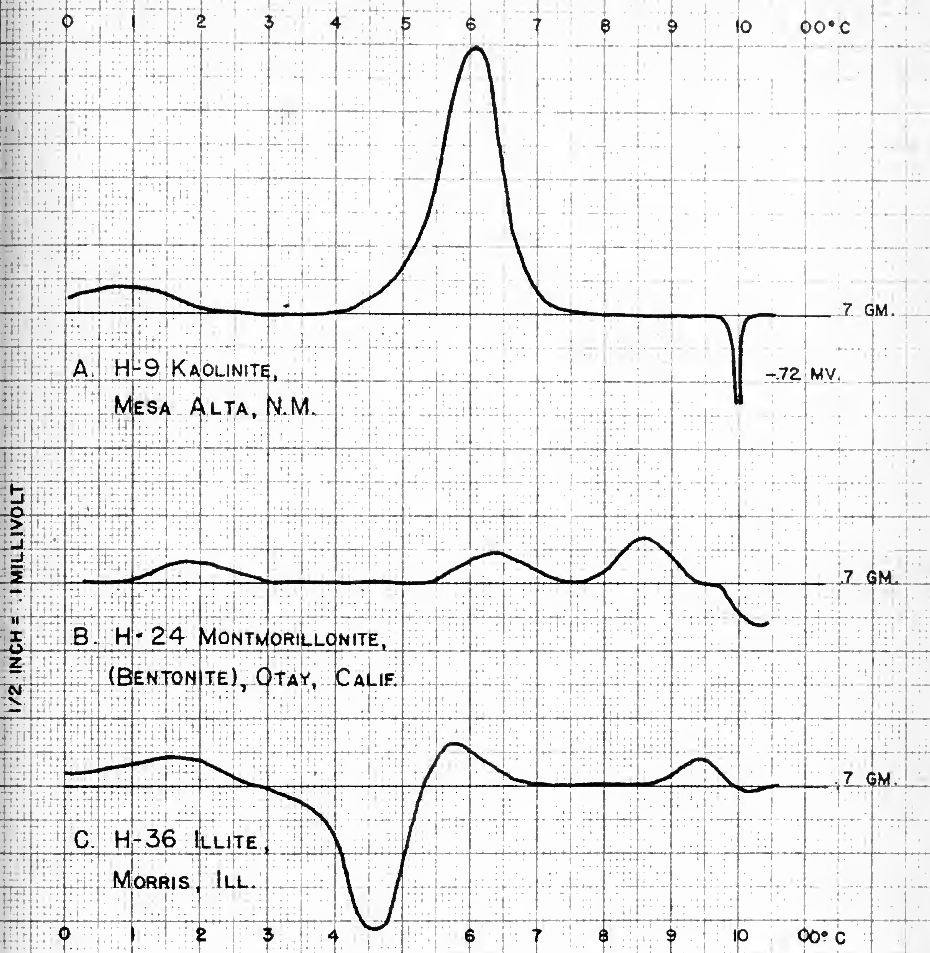
Those problems left unresolved during these investigations have been indicated in this section; recommendations for further, and perhaps improved, study are brought forth in the following section of the thesis entitled "Conclusions and Recommendations".

B. Results of First Series of Tests

Thermal curves of the three natural clay samples used throughout these investigations were established as having no significant dissimilarity when tested in different furnaces. Test runs conducted for each clay sample were reproducible and compared favorably with those obtained by previous investigators. Typical thermal curves obtained in these investigations of the three natural clay samples are illustrated in Figure IX curves A, B and C being for Kaolinite, Montmorillonite (Bentonite) and Illite respectively.

The H-9 Kaolinite used in these investigations exhibited peaks, the magnitude of which, closely approximated those obtained by Harper and Kitterman (10), and Miller (19) for the H-4 Kaolinite. The H-9 Kaolinite gave an initial small endothermic reaction in the low range of temperatures indicating this kaolinite was not of the well crystallized type, as explained under "Theory". The disappearance of this initial reaction was evidenced in those test samples stored in the drying oven for periods approximating two weeks. The prolonged period of drying at 100°C quite obviously drove off the water that had been adsorbed on the crystal layer interfaces.

An observation shared by numerous investigators shows that a prolonged oven drying period prior to testing reduces all the



THERMAL CURVES

NATURAL CLAY SAMPLES

FIGURE IX

endothermic peak magnitudes somewhat. This has been attributed to an instability of the hydroxyl molecules which under long periods of heating are driven off as water vapor. Of particular interest was a reduction of the first endothermic reaction of the montmorillonite (H-24 Bentonite) used in these studies when compared to the much larger reaction obtained by previous investigators at Rensselaer using the same sample clay. The peaks of the first endothermic reaction obtained heretofore were of a magnitude approximately twice the value obtained in these tests. It is apparent that the 100°C drying heat used in these studies drove off most of the lattice water which normally would have remained in the clay under the 40°C drying heat used in previous investigations.

The thermal curve of the H-36 Illite obtained in these investigations is illustrated as curve C of Figure IX. The exothermic reaction attributable to organic matter is evident with peak reaction at 460°C.

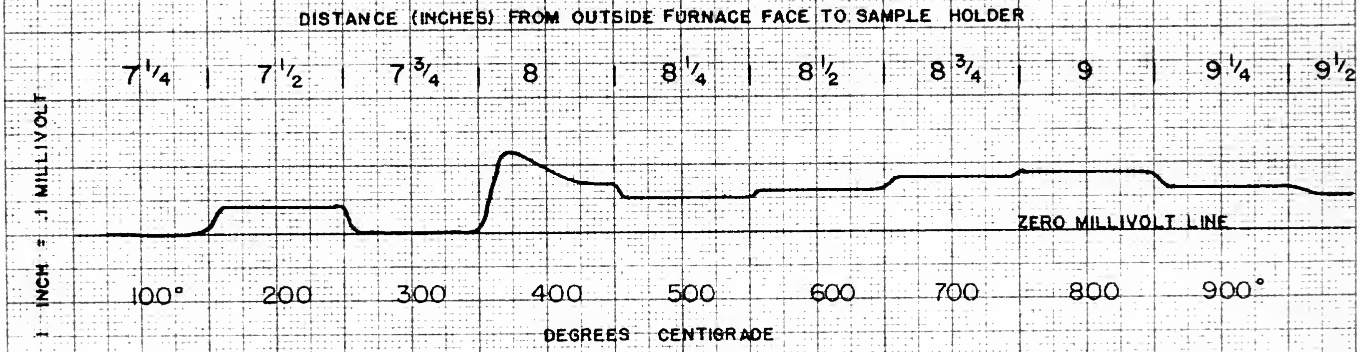
Much has been written by previous authors, with regard to a displacement of the thermal base line. At Rensselaer, Merritt and White (18) and particularly Harper and Kitterman (10) made extensive studies relative to the displacement of the base line and concluded that such a shift was entirely a function of the materials. Harper and Kitterman determined that the state of compaction, volume of material, grain size and other factors governing the thermal conductivity of the materials were responsible for a displacement of base line.

In addition to the above factors, to which a shift of base line

has been attributed, another variable became evident in these studies. The sample holder when placed at different locations within the combustion tube of Furnace No. 1 imparted a displacement of base line locations, all parallel to, but of some constant displacement from the zero millivolt line.

To illustrate the displacement of base line with shift of sample holder in Furnace No. 1, a test run was conducted using inert alumina in each well of the sample holder. The test run began with the back face of the sample holder placed $7\frac{1}{4}$ inches inside the combustion tube where it was allowed to remain until temperature in the furnace had risen to 150°C. A horizontal base line resulted which coincided with the zero millivolt line through the 150° rise in temperature. This is shown in Figure X. At this temperature the holder was carefully slid forward in the combustion tube a distance of $\frac{1}{4}$ inch and the temperature allowed to rise 100° to 250°C. Again the holder was displaced forward $\frac{1}{4}$ inch and the temperature allowed to rise another 100° before further displacement of the sample holder was accomplished. This procedure was continued through a temperature rise of 1000° C where displacement of the sample holder was $9\frac{1}{2}$ inches within the combustion tube. Figure X indicates clearly the results of the movement of the sample holder. Displacements of the base line are evident throughout the test run, shifting simultaneously with movement of the holder and assuming a position parallel to the horizontal zero millivolt line.

These results appear to indicate the existence of "hot spots" in the length of furnace which would impart a difference in



EFFECT ON BASE LINE WITH SHIFT OF SAMPLE
HOLDER IN COMBUSTION TUBE

FIGURE X

temperature to the differential thermocouple and would be reflected on the thermal plot as a constantly displaced base line. It could be reasoned that if no heat variations existed within the furnace the thermal curve of the test run would have indicated no displacement of base line upon movement of the sample holder in the combustion tube. But such was not the case as has been shown above. All subsequent tests conducted in this furnace were done so with the sample holder placed within the combustion tube a distance of 7 3/4 inches. At this placement the base line corresponded to the zero millivolt line.

Base line shift in Furnaces Nos. 2 and 3 was negligible with displacement of the sample holder. Combustion tubes in these furnaces were of the fused silica type as contrasted to cemented alumina in Furnace No. 1. Perhaps this fact would indicate that heat distribution through silica tubes is more nearly uniform than through the alumina type.

After conclusion of these first series of tests wherein necessary familiarization with the operation of equipment had been attained and thermal curves of previous investigators hal been adequately reproduced, it was felt that results to be obtained by further tests would be reliable and subsequently reproducible by future investigators.

C. Results of Second, Third and Fourth Series of Tests

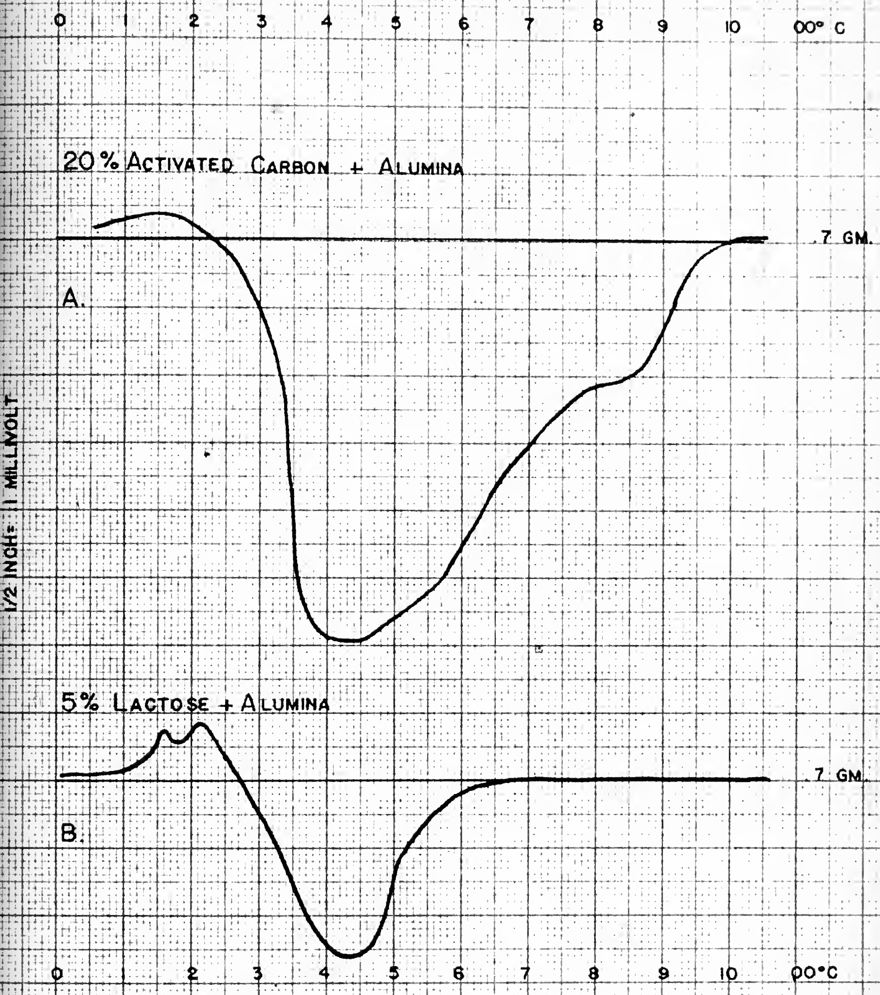
1. General

As indicated in "Procedure", the series of tests for the second, third and fourth phases were run concurrently in order to

efficiently use all furnaces. These test phases included the testing of natural clay samples in vacuum (Test Series No. 2) and the tests on mixtures of clay samples with organic matter under atmospheric conditions and under vacuum (Test Series Nos. 3 and 4). Many of the results obtained in these tests were interrelated and, therefore, presentation of the results and discussions of these test phases together in this subsection appears expeditious.

Results of first experiments under normal atmospheric conditions using mixtures of carbonaceous matter indicated that small amounts of organic materials would be sufficient to produce easily recognizable thermal reactions as plotted on the thermal curve. A mixture by weight of 20% activated carbon and 80% alumina produced the thermal curve illustrated by Curve A of Figure XI. It is to be noticed that the reaction of activated carbon in these quantities is a deep exothermic (oxidation) reaction extending in range from 200°C to 800°C.

A mixture by weight of 20 percent lactose and 80% alumina produced vigorous burning under atmospheric conditions sufficient to discharge test sample material from the sample well. A mixture by weight of 5 percent lactose was determined to be optimum since large characteristic reactions were obtained without vigorous burning. Thermal curve B of Figure XI illustrates the reactions of 5 percent lactose with alumina under normal atmospheric conditions. The curve is unique among those organic materials used in these investigations for there appears in the early ranges of temperatures an endothermic peak of jagged shape. This is associated with the melting point of lactose which occurs at 202°C. A melting reaction would be



THERMAL CURVES

CARBONACEOUS MATTER

FIGURE XI

endothermic in nature and would confirm the reactions recorded in this test run. An exothermic reaction follows and extends to 550°C where oxidation is complete. For uniformity and comparison purposes all mixtures used in these investigations were set at 5 percent by weight of organic material to 95 percent of natural clay sample.

As a result of vacuum application to the combustion tube it became necessary to show extra care in packing all materials in the sample wells. Several test runs were found to be of no value when it was noticed that test materials were drawn out of the sample wells during vacuum operations leaving thermocouples bared. Observations proved that immediately after application of the vacuum to the combustion tube, material not carefully packed was partially pulled out of the wells. Remedial action included covering of the test materials which was explained in more detail under "Procedure".

During the concurrent investigations of the three test series thermocouple breakage became a major problem. Most of the breakage was occurring at those portions of the thermocouple leads which were not covered by the porcelain insulators. A minor amount of the breakage occurred at the bead itself. Thermocouple life is not indefinite, it is recognized, but no mention was made of excessive thermocouple breakage by previous investigators here at Rensselaer or by others elsewhere. Many thermocouples were lasting through one or two runs only, several breaking on the initial run. Most other investigators use No. 22 gage wire for chromel-alumel thermocouples which is lighter wire than the No. 18 gage wire used here. Therefore, it seemed quite apparent that breakage was not due to the use of too light a wire in the differential thermal process.

Consideration was given to the manner in which thermocouples were made. Previous investigators had used thermocouples made by electric arc methods and experienced no serious breakage problems. A switch to use of thermocouples made by the electric arc method instead of the d.c. carbon arc produced no better results under test conditions. It had been reasoned that any borax flux inadvertently left on the thermocouples during the fusion process could conceivably act as a reducing agent and deteriorate the thermocouple wire. As indicated above, test runs conducted using the newly-made thermocouples experienced breakage as frequently as before. This unexplained malfunction of thermocouples prevented the accumulation of usable data for a period of over three weeks during which time thermocouples were being made, calibrated, assembled in holders and subjected to test conditions which caused almost immediate breakage.

It was noted that a majority of thermocouple failures was occurring in those furnaces operating under vacuum. Reference to thermocouple handbooks uncovered a statement to the effect that chromel-alumel thermocouples were subject at high temperatures to rapid deterioration in a reducing atmosphere such as sulphur, hydrogen, or carbon monoxide. Reasoning indicated that under vacuum operations wherein the vacuum is admitted to be imperfect, carbon monoxide will form as a result of carbon burning in insufficient oxygen supply. Because the vacuum pump was required to be operating continuously, leakage was prevalent. The limited amount of oxygen in the air leakage was reasoned to be forming carbon monoxide with the carbonaceous matter added to the clay mixtures. The corrective action which was taken to minimize the effects of any

carbon monoxide present in the combustion chamber resulted in solution to the problem of thermocouple failure. Remedial action included the use of inert gasses as an enclosing atmosphere to substitute for vacuum. Operation under inert gasses gave promise of a more nearly air-free atmosphere. (The advantages derived and results obtained through use of inert gasses are discussed in the succeeding subsection, "Results of the Fifth Series of Tests.")

Tests under vacuum were continued with certain action being taken to lengthen the life of thermocouples used. Assembled sample holders were heated to maximum test temperatures to allow a protective oxide coating to form on the thermocouple leads. It was reasoned that the oxide coating would protect the thermocouple leads from the reducing action of the carbon monoxide. The practice followed thereafter was to make four or five test runs under vacuum(or inert gasses)in which carbonaceous matter was present and then again heat the assembled sample holder to maximum test temperatures under normal atmospheric conditions to allow the thermocouple wires to reoxidize. In view of consideration given to the possibility that carbon monoxide was causing the failure of thermocouples, a limitation to 5 percent by weight of organic material in test samples was in keeping with attempts to lessen the carbon monoxide effect. It was also decided to limit test runs to a maximum temperature of 1050°C in the interests of preventing excessive thermocouple exposure to dangerously high temperatures. Some previous test runs had been conducted through 1100°C. Since the identifying thermal reactions of materials used in these investigations were completed prior to 1050°C the extra range

of temperature was essentially of no value. The higher temperature range served only to deduct from the useful life of the thermocouples. Succeeding test runs conducted under vacuum and under inert gasses proceeded without interruption due to thermocouple failures.

2. Examination of Vacuum Thermal Curves

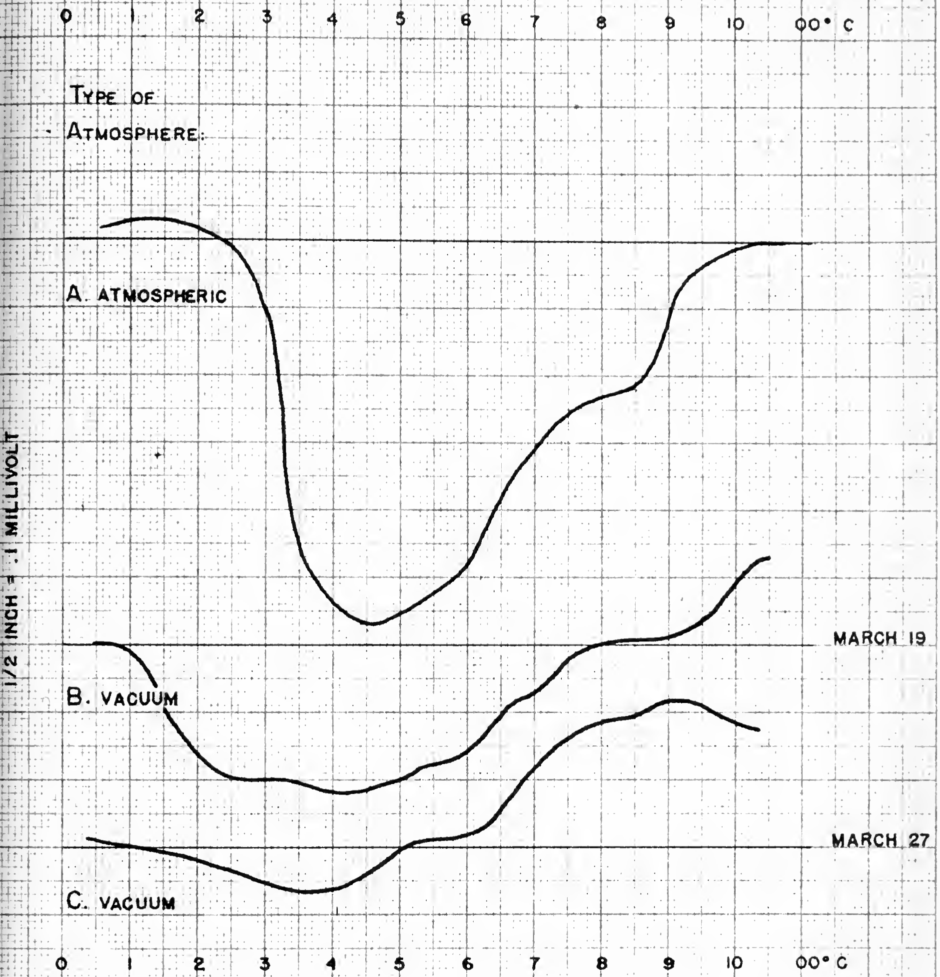
In general thermal curves produced under vacuum operation were erratic and gave variable results. However, some indication was given of a reduction, if not an elimination, of thermal reactions due to carbonaceous matter. The reliability of the interpretation placed on these curves could be of a limited value only, it was determined. Thermal curves under vacuum were not strictly reproducible as has been the case of operation under atmospheric conditions. Curves produced during the initial test runs were found to vary somewhat with those obtained at later stages of vacuum operation. The shift of base line, which is commonly encountered and satisfactorily explained by those authors investigating under atmospheric conditions, was greatly magnified in these operations under vacuum.

Thermal reactions themselves were magnified and somewhat elongated. Though these reactions tended to complicate the interpretation of vacuum thermal curves, there were nevertheless those characteristics which appear to indicate a feasibility of the vacuum operation. Some thermal reactions observed in these operations tended to agree with theorized expectations and will be indicated when reference to illustrated vacuum thermal curves are introduced.

Figure XII is included to illustrate the effect of vacuum when a test run was conducted on a mixture of alumina plus 20 percent activated carbon. (These runs were made prior to the decision to reduce the organic material to 5 percent by weight of material tested. For the same reason, several other illustrated test runs which follow also contain greater than 5 per cent organic matter.)

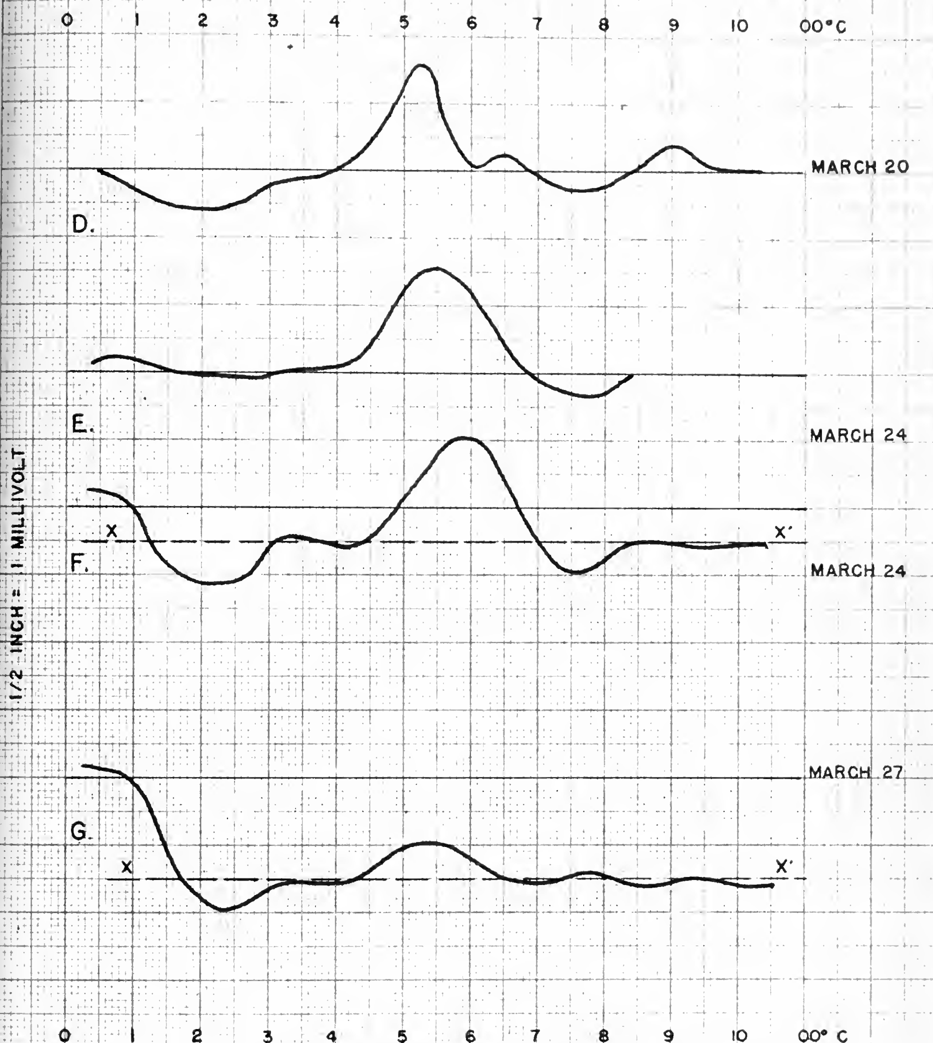
Thermal curve A, of Figure XII is of the alumina-activated carbon mixture and exhibits a large exothermic reaction which ranges from 200° - 900°C. This test run was conducted under atmospheric conditions and gives indication of the large expanse of the thermal range which is covered by the oxidation of the moderate degree of carbonaceous matter in mixture. Curves B and C of the same figure illustrate thermal curves obtained for the same mixture under vacuum conditions. Both curves illustrate a reduction of the oxidation of organic material. This would be expected under conditions in which air in the system was reduced but not eliminated. In the upper ranges of temperatures of both thermal curves, there is indicated a growing endothermic reaction, of which curve C exhibits the greatest. Reasons for this shift from exothermic to endothermic reactions are not known and can only be surmised. By comparison with curve A, where the carbon was oxidized in atmosphere, reactions under vacuum indicate a definite lowering of the intensity of the oxidation reaction. However, liberal interpretation of these curves would be necessary to ignore the unexplained variations of the thermal curve in the higher ranges.

Four thermal curves for illite tested under vacuum are illustrated in Figure XIII. Curve E has been plotted only to 800°C



Alumina + 20% Activated Carbon

FIGURE XII



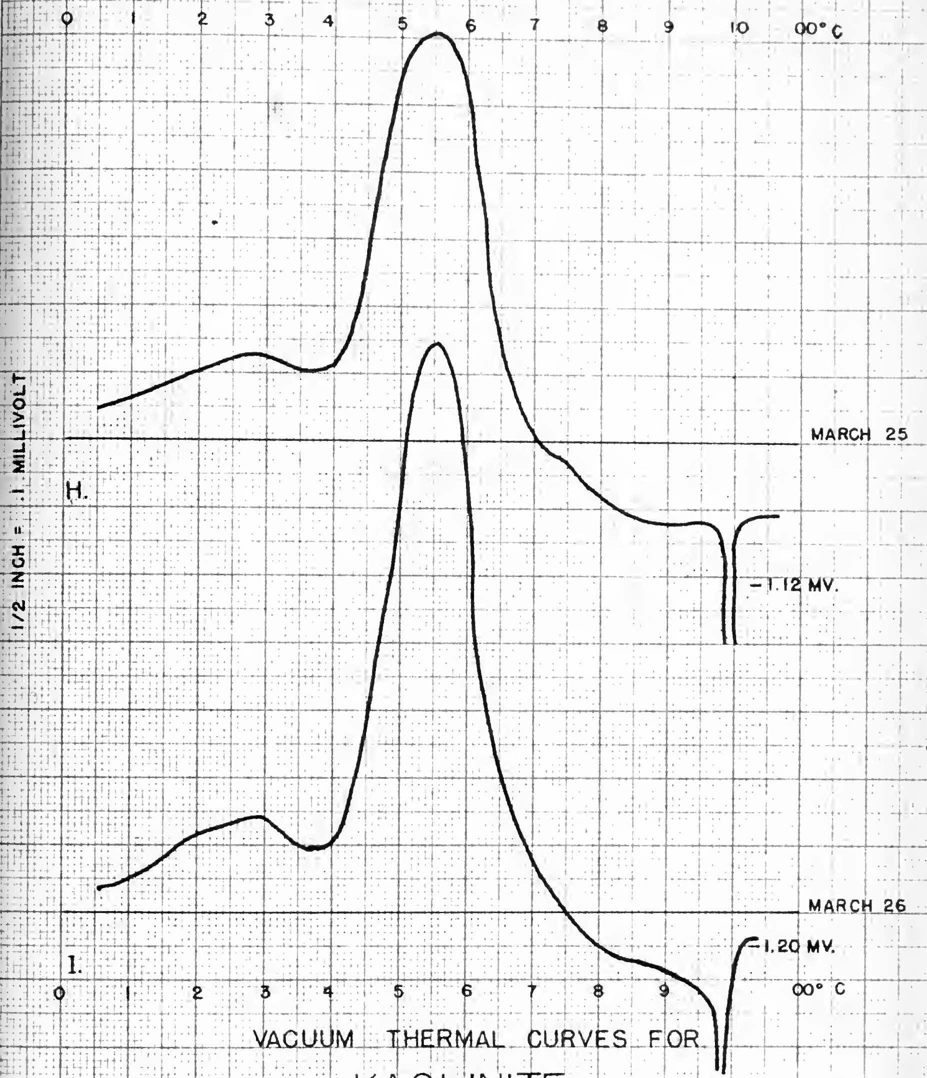
VACUUM THERMAL CURVES FOR

ILLITE

FIGURE XIII

as it was at this point during testing that the differential thermocouple broke. These curves illustrate that only a small amount of reliability can be placed in these curves since in the upper ranges the curves oscillate from exothermic to endothermic reactions. As was typical of curves in Figure XIII, only a small similarity to illite curves under atmospheric conditions is noted. Consideration must be given to curves F and G which indicate displaced base lines of quite large magnitude (illustrated by dotted line X-X'). It is to be expected that the exothermic reaction attributable to the oxidation of organic matter which occurs at 460°C would be eliminated under vacuum operation. Curves E, F and G do not exhibit this exothermic reaction, when it is accepted that the base line in F and G is displaced as shown. Here again liberal interpretation of the thermal curves must be employed to obtain expected reactions. In the higher ranges of temperature oscillation of the thermal curves across the base line is again indicative of unreliability of the curves in these ranges. The endothermic reaction between 500°C and 600°C characteristic of all these illustrated curves could be attributable to the second endothermic peak of illite. However, the dimensions of the reaction is greatly amplified over standard illite curves.

Figure XIV illustrates two thermal curves of kaolinite under vacuum. The thermal reactions demonstrated herein have definite variations from that obtained under atmospheric conditions and illustrated in Figure IX, Curve A. Thermal curves under vacuum indicate magnified peak reactions and a double displacement of base line. The early portion of the thermal base line is displaced in the endo-



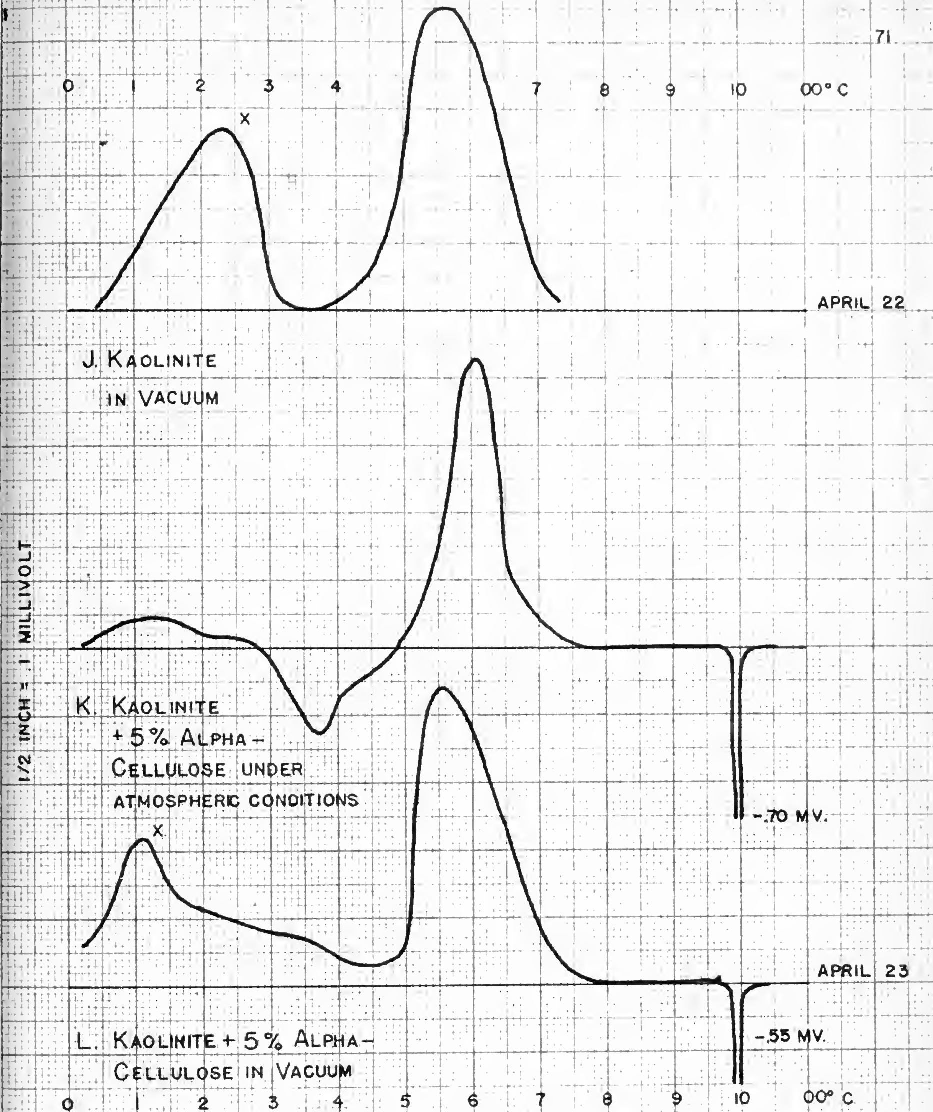
VACUUM THERMAL CURVES FOR

KAOLINITE

FIGURE XIV

thermic direction the later portion of the curve is displaced in the exothermic direction. Grim (6) indicates that double displaced base lines, similar to that exhibited by the kaolinite under vacuum would be characteristic of a sudden change in physical state where the heat conductivity of the newly-formed substance is radically different than before the reaction. Such a reaction in kaolinite is not indicated under atmospheric conditions and it would seem improbable under vacuum. The cause for this double displacement of kaolinite in vacuum is unknown. Another detail exhibited by these kaolinite thermal curves shows occurrence of the endothermic peak about 550°C as compared to the 600°- 610°C peak value given under atmospheric pressures. The earlier occurrence of the endothermic reaction under vacuum would indicate an earlier departure of the hydroxyl molecules from the kaolinite crystal lattice in the form of water vapor. The reduced air pressure of vacuum operation may allow hydroxyl water vapor to escape at earlier temperatures since the water vapor would not have to overcome atmospheric pressure in its escape.

The displacement of the base line noted in the vacuum thermal curves was determined to be a function of the operation of the vacuum pump. While the vacuum pump was in operation the base line was shifting and oscillating; when the pump was turned off, the thermal curve immediately sought to return to the normal base line. Thermal curves J and L of Figure XV indicate this clearly. During the conduct of both these test runs the vacuum pump was shut off at points marked "X" on Figure XV, while the base line was shifting. The system was maintained closed by clamps securely tightened on the



EFFECT OF SHUTTING OFF VACUUM DURING TEST RUNS

FIGURE XV

vacuum rubber tubing. Note the immediate shift of curve toward the zero millivolt line and the resulting characteristic thermal curve of kaolinite. The test run illustrated by curve L contains organic matter in the form of alpha cellulose. After the vacuum was shut off and the thermal curve shifted back to the zero millivolt line no indication of an exothermic reaction was evident. Thermal curve K is representative of kaolinite containing alpha-cellulose and shows the exothermic peak at about 375°C which is the oxidation reaction of the organic alpha-cellulose. It would appear that the partial vacuum remaining after point "X" eliminates the greater portion of oxidation reaction evidenced in curve K. This is a large organic reaction and its disappearance appears obvious by comparison of thermal curves. Had only small amounts of organic material been present in the clay sample, difficulty would have been experienced in evaluating the elimination of its reaction due to the shifting base line which occurs during this range of temperatures.

In the test run illustrated by thermal curve L, a pressure rise occurred after vacuum operation ceased which saw the pressure increase from .5 mm of mercury absolute pressure to above the 5 mm pressure, the greatest reading of the gage, in a space of five minutes. It was suspected the leakage occurred at the tube itself and a check of the vacuum system exclusive of the combustion tube verified this. Vacuum applied to the system and then isolated by clamps from the vacuum pump and the combustion tube was maintained for ten minutes above 3 mm. of mercury absolute pressure.

It is to be noted in the vacuum thermal curves presented in the preceding illustrations that curves become increasingly erratic

and unreliable when examined in chronological order. Each curve has been dated for comparison purposes. In the earlier curves the base line is nearer to the horizontal, the effect of displacement is not nearly as great, resulting in curves that tend to be more characteristic of expected results. This fact would indicate a continuously worsening condition through continued operation of the system. Coupled with the known fact that there exists greater leakage in the combustion tube than in the remainder of the system it would seem that air leakage could exist through the combustion tube itself. A leakage of air into the combustion tube which could result in uneven cooling effects to the sample holder may cause the wide shift and wavering instability of the base line. It is a certainty that when the vacuum is shut off and the attempt is made to maintain the applied vacuum, there results a definite return of the base line plot to its normal position. This could support the postulation that the continued application of vacuum to the system during test runs causes air flow of some degree within the combustion tube. Further, the air flow may be the cause of the variations of the thermal plot under vacuum.

A supporting argument to the theory of combustion tube leakage is a discussion from Seybolt and Burke (22) concerning the fused silica material of which the combustion tube is made. Their evaluation of the fused silica tube is as follows: "Silica or sand crucibles are subject to two drawbacks which are serious enough virtually to eliminate them as serious contenders for an important place in the metals laboratory. One is polymorphic transformation at 573° and 870°C where low quartz passes to high quartz and then to

tridymite, respectively. These transformations are accompanied by substantial volume changes which tend to crack the crucible on heating or cooling.

Fused silica could not be used at temperatures higher than 1100°C and then only for short periods of time. It is better to limit the temperature to 1000°C. Long exposure even at 1000°C results in devitrification caused by transformation of the amorphous silica to the crystalline crystobalite with an accompanying volume change. This change to a crystalline form of quartz results in a chalky structure which is very weak and porous".

The gradual change described above of the fused silica to the crystalline form of quartz through continued operations at the higher ranges of temperatures appears to substantiate the suspicions of the occurrance of air leakage into the tube. Certainly the ranges of temperatures reached in differential thermal analysis are those detrimental to fused silica. The gradual change described by Seybolt and Burke, of the fused silica to a weak, porous material when subject to temperatures of 1000°C or more would explain why thermal curves obtained in the initial stages appeared more reasonable than those conducted at later dates. In the earlier test runs the combustion tube would have been more nearly air tight and the effects of air leakage would have been to a lesser degree.

Further it would seem pertinent to mention that under conditions of an evacuated atmosphere such as was present in these investigations the effects of heat radiation will become increasingly important. Whether the effect of possible uneven heating reflected by heat radiation to the sample holder could cause detrimental effect to the

thermal curves is not known but they are mentioned here as being a possible clue to the unreliability of the vacuum technique under present testing procedure. The author regrets that there was not sufficient time to explore further into this technique of the differential thermal analysis. As indicated previously, a fresh approach to the problems encountered in these studies may quickly and simply solve that which appeared quite difficult and perplexing at this time. Recommendations for further study of the vacuum technique are properly covered in the "Conclusions and Recommendations" section of this thesis.

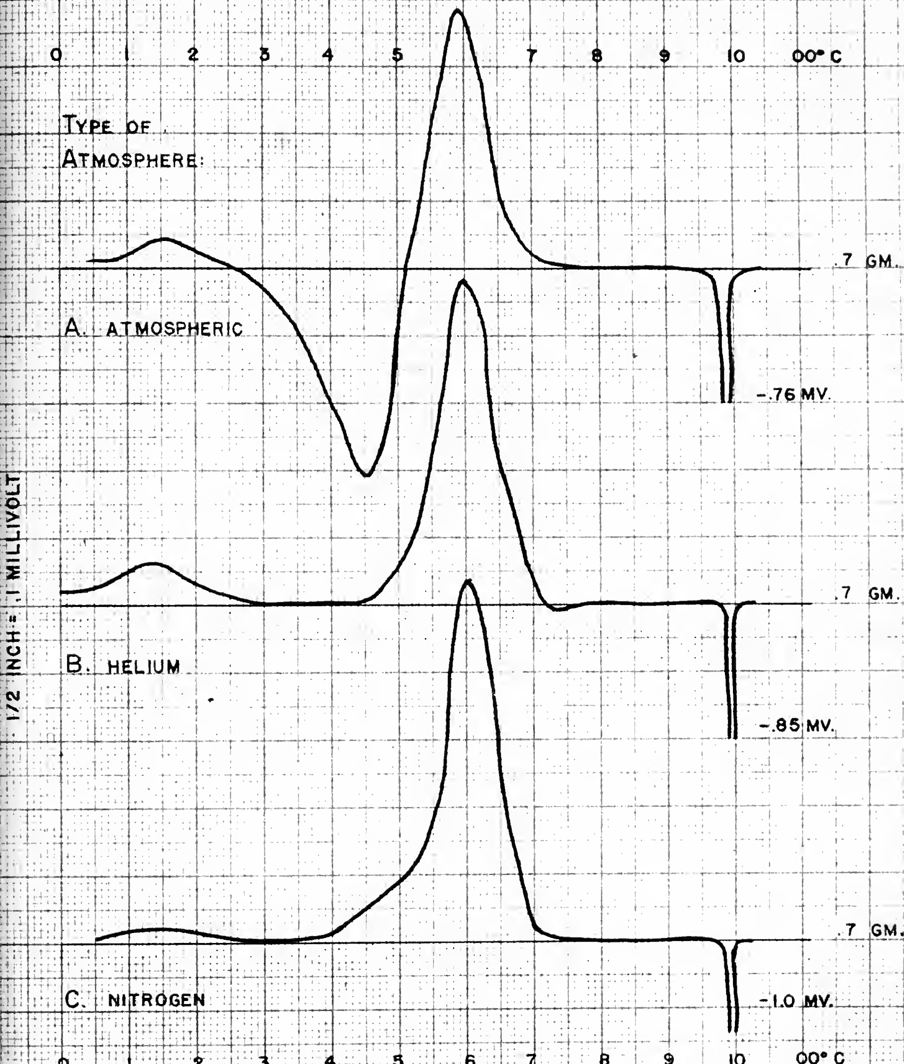
D. Results of Fifth Series of Tests

In view of the erratic results obtained in the vacuum process as has been indicated in the foregoing section it was decided to search for a more positive method of obtaining the desired results. The introduction of inert gasses into the combustion tube during thermal analysis was employed in the fifth series of tests as a substitute for vacuum. In the results of the fifth series of tests was realized the solution to the problem as was stated in the forward sections of this thesis. The use of inert gasses as an atmosphere in which to conduct differential thermal analysis was effective in the expulsion of air from the combustion tube. In the absence of air the thermal reaction which had been characteristic of the organic material when heated under atmospheric conditions was eliminated. This will be shown by examination of the thermal curves presented in paragraphs to follow.

Thermal analysis under inert gasses seemed to offer certain advantages, practical and theoretical, over the vacuum technique.

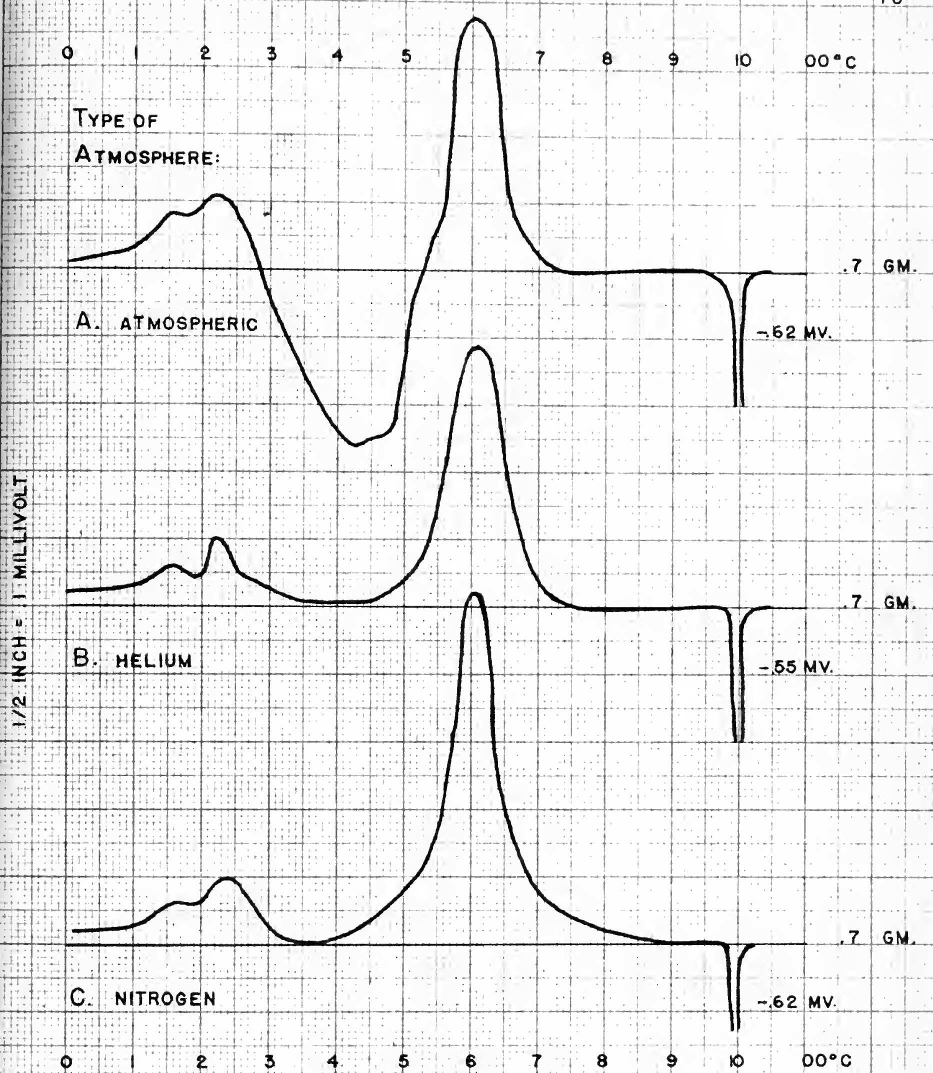
In the practical sense, the process of differential thermal analysis under an atmosphere of gas was an easier operation. The elaborate precautions necessary to maintain an air tight system under vacuum operation were not strictly required when gas was used. Inert gasses were introduced into the combustion tube under pressures sufficient only to maintain flow of gas through the tube. Gas pressures of one pound or less above atmospheric maintained steady flow. Therefore, any leakage which may have taken place in the system was outward flow instead of inward into the system. Small leakage in this manner was desirable since outward leakage prevents air from entering the tube and at the same time carries out of the tube a portion of any remaining air which might be present. Theoretically, then, the test chamber atmosphere would become more nearly that of the pure inert gas and would contain less oxygen as operation progressed. This is an advantage over the vacuum system where continuous vacuum pump operation was drawing fresh air into the system providing oxygen with which carbonaceous matter could combine under test temperatures.

Thermal curves indicating the results of the imposition of the inert gasses of helium and nitrogen to the test chamber during differential thermal analysis are shown in Figures XVI through XXVI. In each figure is shown the thermal curves of a standard clay sample which has been mixed with 5 per cent by weight of a named organic material. Two clay samples, the kaolinite and the montmorillonite (bentonite) were mixed individually with each of the five organic materials to provide the comparison curves of the ten test mixtures. Thermal curve A on each figure is the result of test runs conducted under atmospheric conditions. The exothermic reaction which resulted



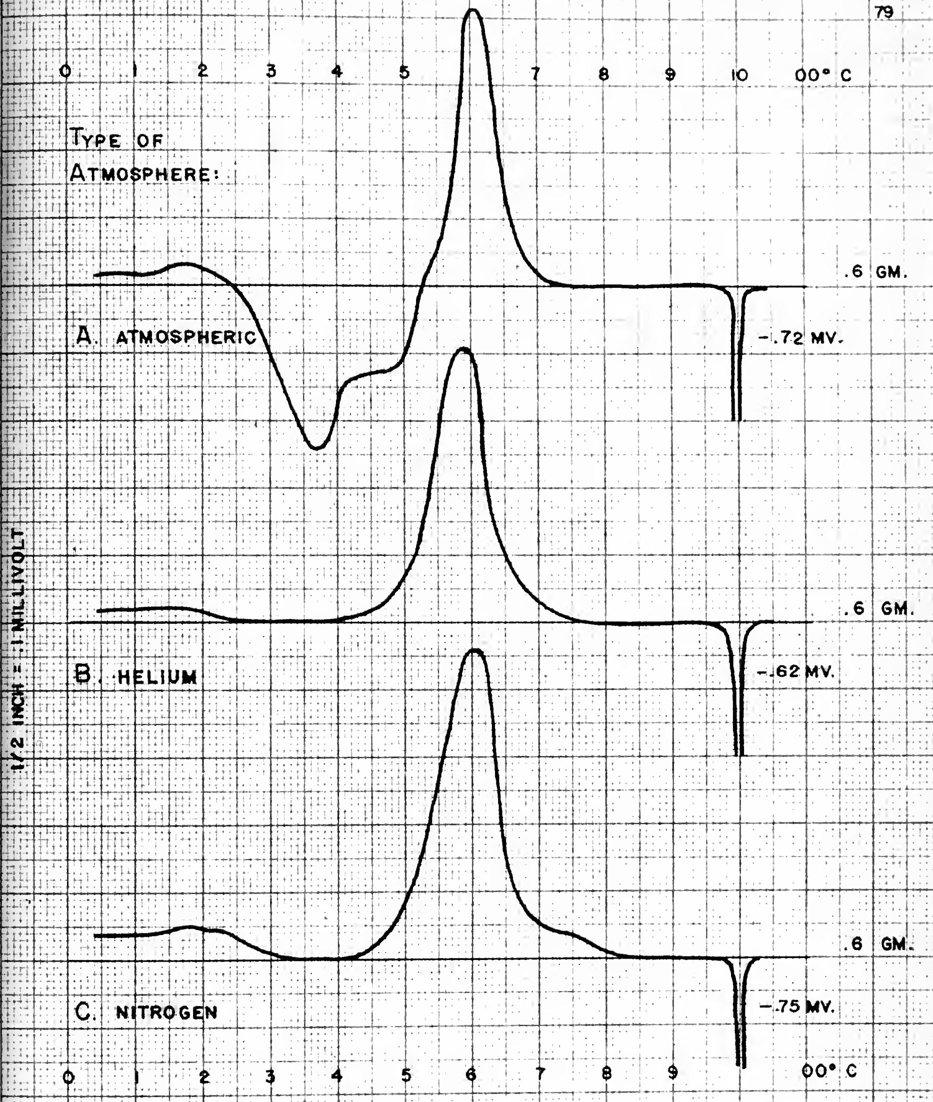
KAOLINITE + 5 % ACTIVATED CARBON

FIGURE XVI



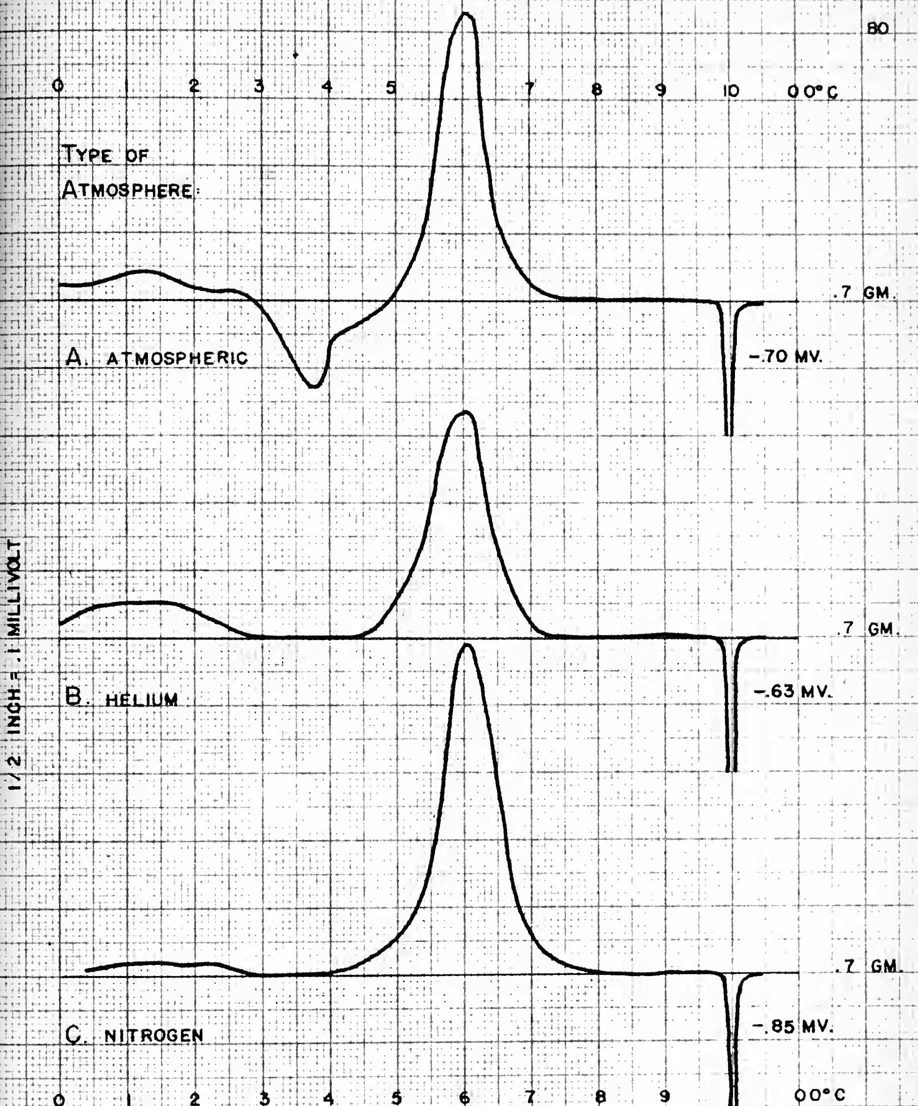
KAOLINITE + 5% LACTOSE

FIGURE XVII



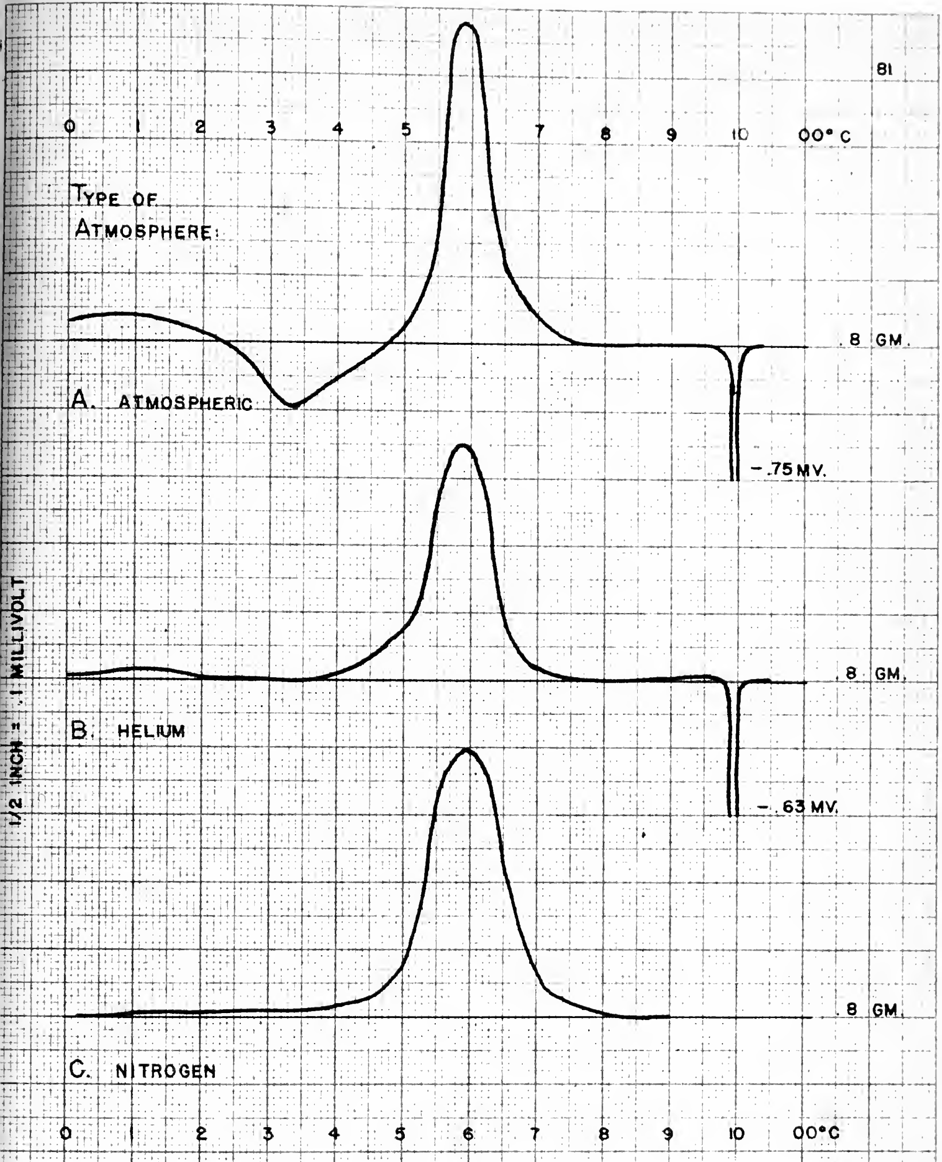
Kaolinite + 5% Wood Flour

FIGURE XVIII



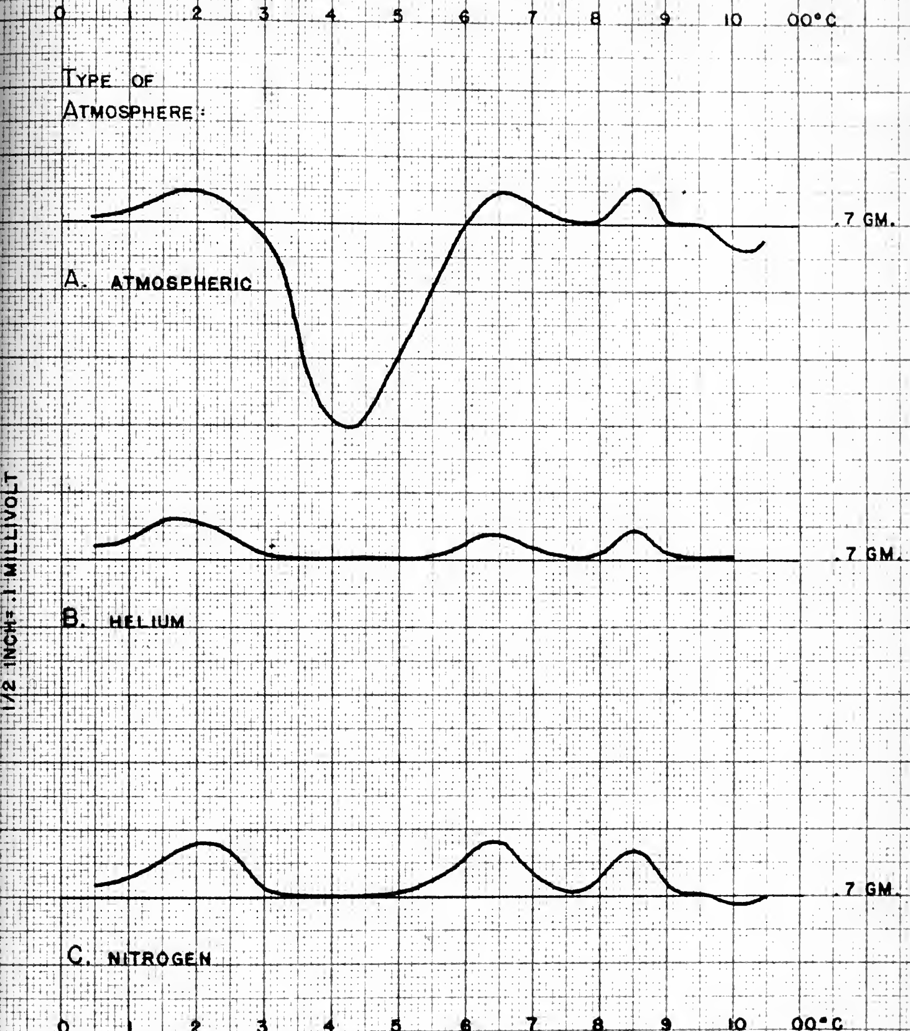
KAOLINITE + 5% ALPHA-CELLULOSE

FIGURE XIX



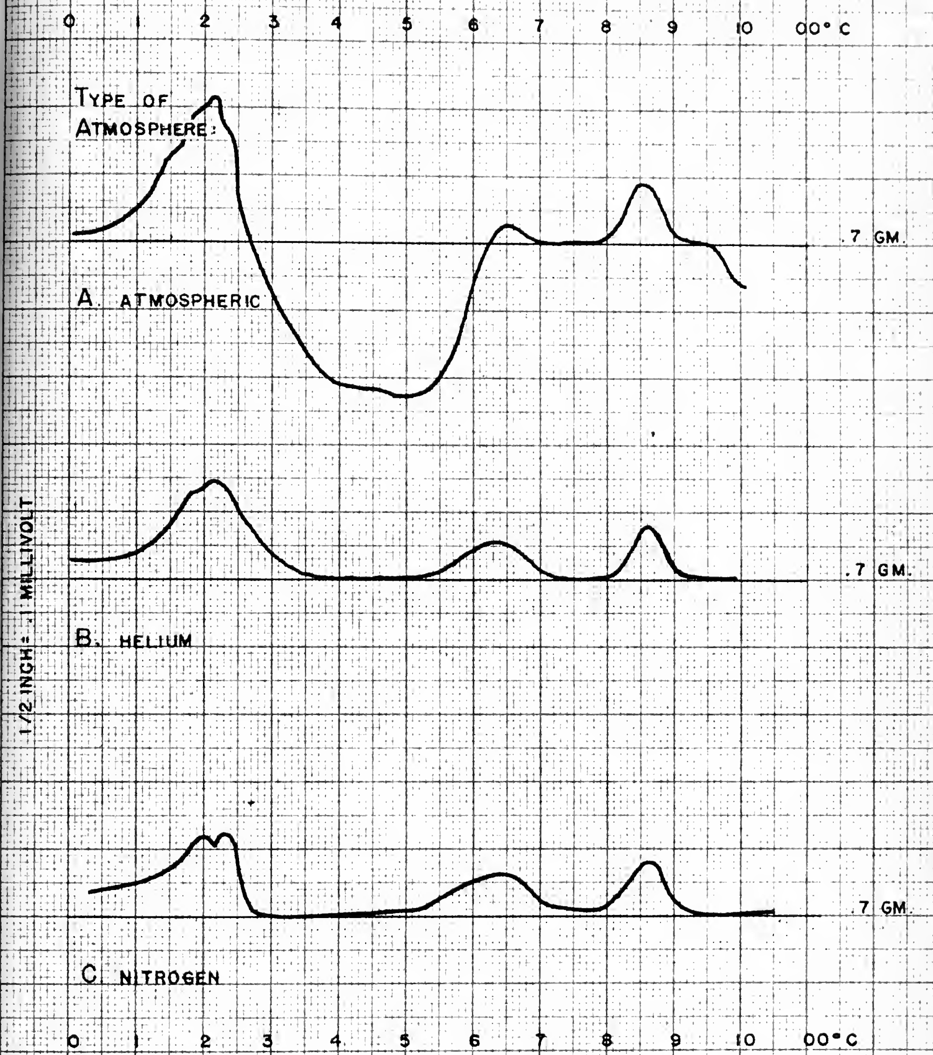
KAOLINITE + 5% SEWAGE SLUDGE

FIGURE XX



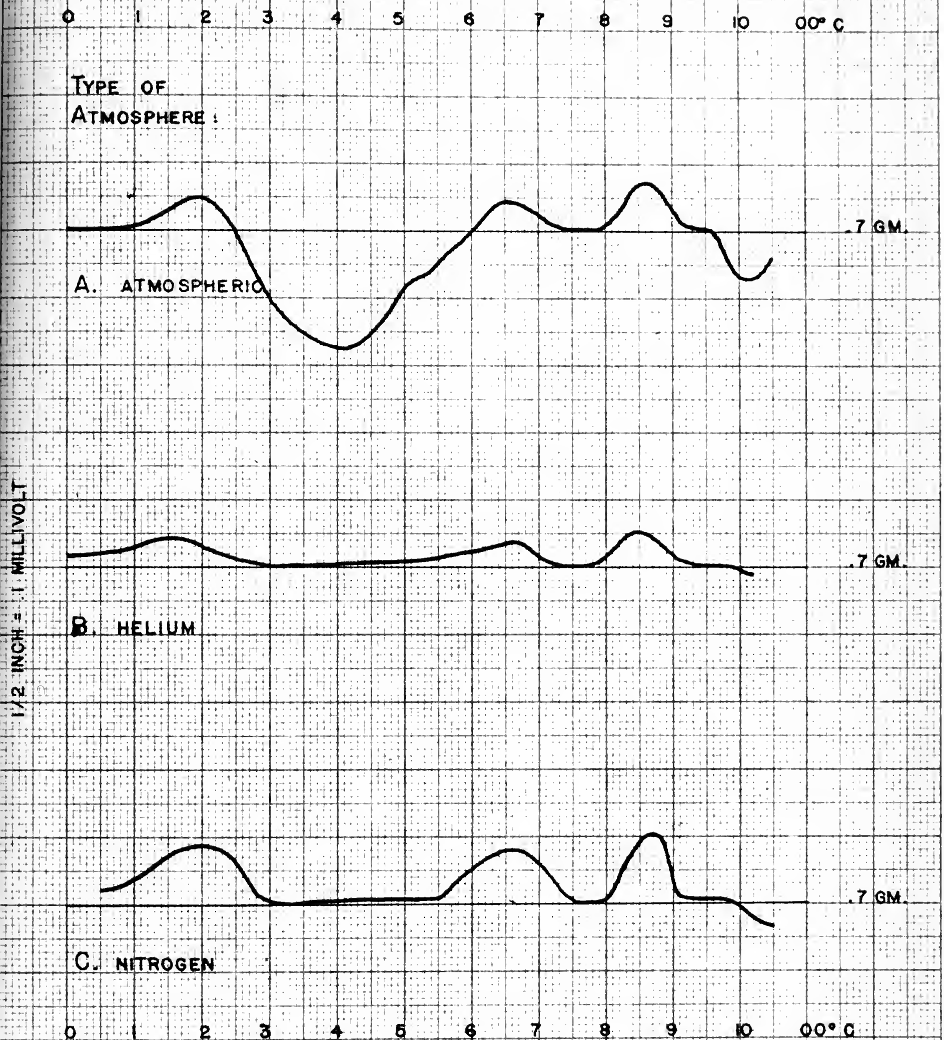
MONTMORILLONITE + 5% ACTIVATED CARBON

FIGURE XXI



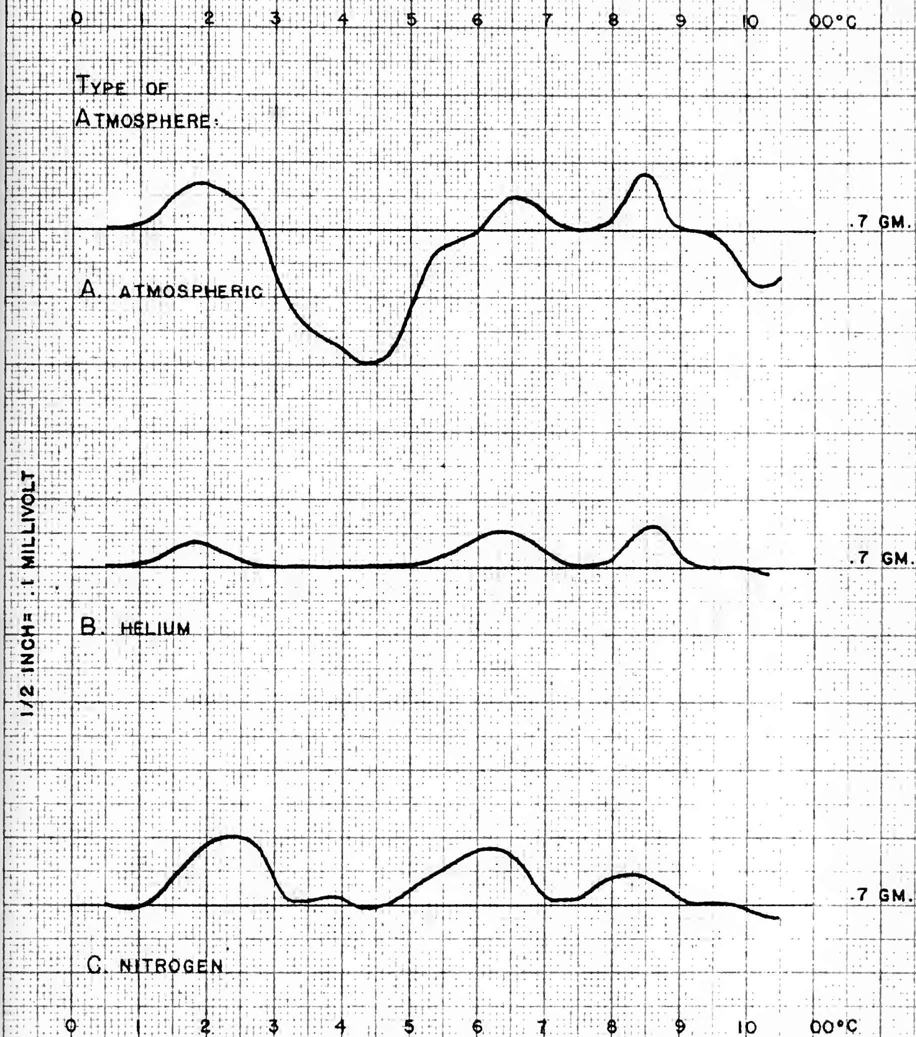
MONTMORILLONITE + 5% LACTOSE

FIGURE XXII



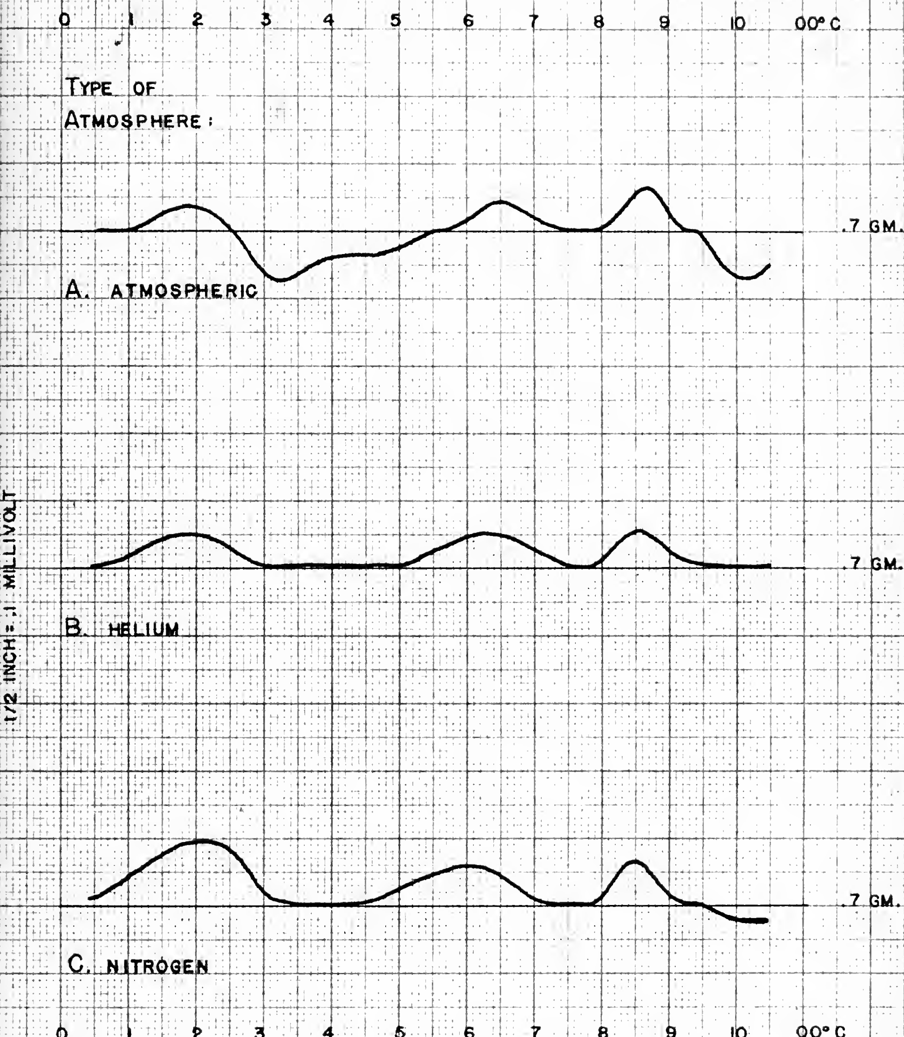
MONTMORILLONITE + 5 % WOOD FLOUR

FIGURE XXIII



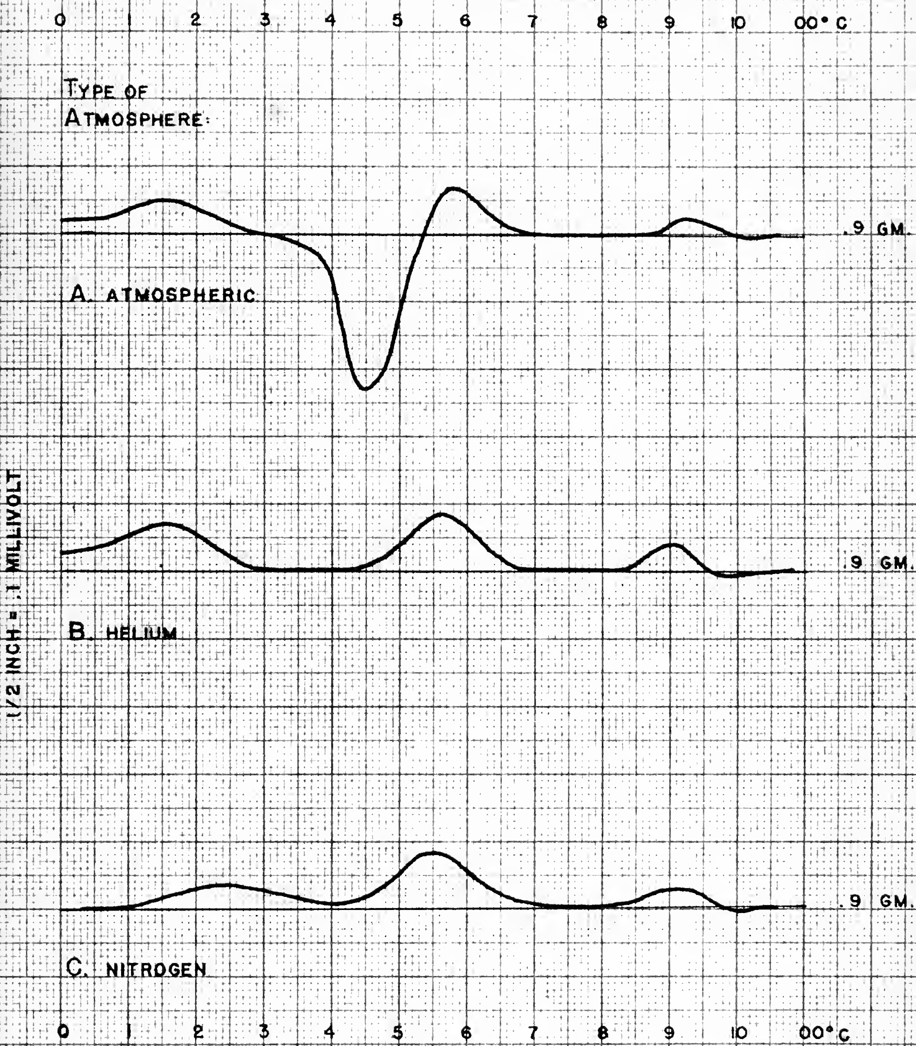
MONTMORILLONITE + 5% ALPHA - CELLULOSE

FIGURE XXIV



MONTMORILLONITE + 5% SEWAGE SLUDGE

FIGURE XXV



H-36 Illite, Morris, Illinois.

FIGURE XXVI

from the burning of organic materials should be noted. This reaction in most mixtures is large in peak magnitude and extends generally through the range of temperatures 200' - 550°C.

Curves B and C in each figure are those conducted on the same mixture of clay and organic material when tested under conditions of helium and nitrogen atmospheres, respectively. It is to be noted that the exothermic reaction of the organic material, which was prevalent in Curve A has been completely eliminated in all cases of operation under the inert gas atmosphere.

In the case of clay samples mixed with lactose, the endothermic reaction due to melting of lactose at 202°C appears in all thermal curves A, B and C, since this melting reaction is a function of temperature alone and the atmosphere of helium or nitrogen could have no effect.

The thermal curve for H-36 Illite, Morris, Illinois is included as Figure XXVI. Examination of these thermal curves indicate that under the inert gas atmosphere the organic material which characterizes this illite and exhibits a peak reaction at 460°C has been effectively removed. The standard curve for illite remains, the peak reactions of which are neither masked or eliminated by the organic material.

A comparison study of the thermal curves A, B and C of Figures XVI through XXVI with each other and with curves for the standard clay minerals shown in Figure IX indicate that the organic material included in the standard curves tend to mask the forward slope of the endothermic peak in the 500° - 600°C range. This would be due to the countering effects of the exothermic oxidation reaction of the carbonaceous material and the endothermic reaction of the clay sample. Greater amounts of organic material present could conceivably eliminate the clay reaction completely and thereby hinder

its proper identification. When samples including organic material are tested under helium or nitrogen, the original shape of the endothermic peak returns.

The disappearance of the organic material from the test sample without recorded thermal reactions in tests conducted under inert gasses most likely is a pyrolytic effect. Pyrolysis is a chemical decomposition of low heat exchange occurring over long ranges of temperature. Residue of tested samples of clay and activated carbon was blackened in appearance indicating at least a partial retention of the carbonaceous material perhaps in chemical union.

With reference to the thermal curves of montmorillonite and mixed organic material which are illustrated in Figures XXI through XXV an interesting observation has been noted. The usually large characteristic exothermic reaction for this montmorillonite which occurs at approximately 1000°C under atmospheric conditions appears to be much reduced in magnitude or eliminated entirely when tested under atmospheres of helium and nitrogen. Investigators attribute this exothermic reaction to the formation of beta-quartz. The existance of beta-quartz after firing montmorillonite above 1000°C was confirmed by J. E. Powell who was doing thesis work with x-ray diffraction. Samples of montmorillonite tested beyond 1000°C under inert gas were likewise confirmed to be beta-quartz by x-ray diffraction methods. Thus, x-ray diffraction analysis indicated no difference in end product resulted through separate techniques of thermal analysis. This leads to the apparent belief that there was a slow transformation to beta-quartz at these temperatures which was registered only as a slight reaction or not at all. The reason for the slower transformation of structure in the absence of air is unknown. Grim

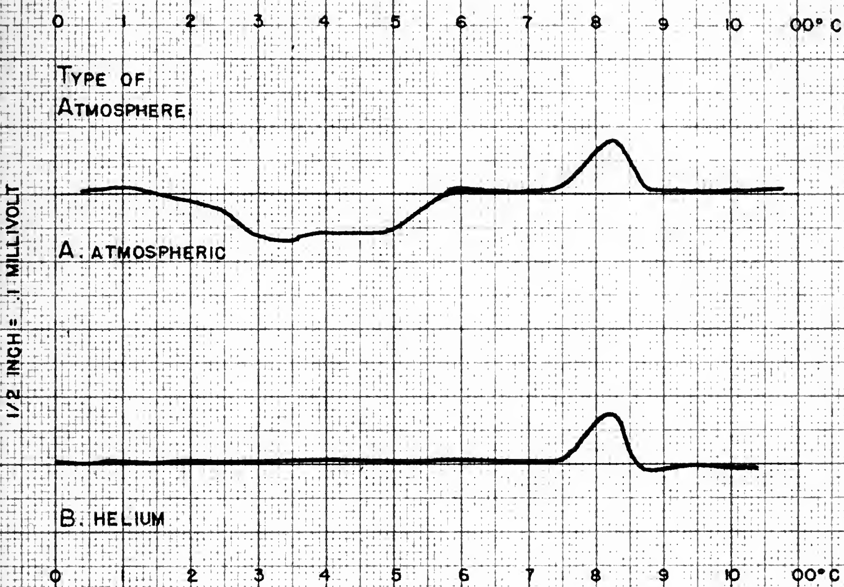
postulates that extra oxygen atoms are needed in the crystal structure of beta-quartz when it changes to form cristobolite at temperatures closer to 1100°C. However, tests of the montmorillonites in these investigations were not carried to 1100°C and the X-ray diffraction analysis indicates beta-quartz as the end product of this author's test runs. The reason for the reduction or elimination of the exothermic reaction under inert gasses technique when montmorillonite transforms to beta-quartz at 1000°C is unknown.

E. Identification of St. Lawrence Seaway Material

Two soil samples were supplied by Professor E. J. Kilcawley to this author and to J. E. Powell for cooperative identification purposes. The material, originally furnished from the St. Lawrence Seaway project, was greenish-brown in color and was of clay-sized material.

Thermal curves for these materials were identical and curves presented in Figure XXVII are illustrative of both samples. There is exhibited one large endothermic peak in the 810°-835°C temperature range followed immediately by what appears to be a slight exothermic peak. Another endothermic peak, although small, appears in the 575°-590°C range of temperature. Small exothermic reactions appear in the broad range of temperatures between 150°-550°C and by testing under helium were found to disappear. This indicated the presence of a small amount of organic material.

The large endothermic reaction in the higher ranges of temperatures show close similarity to the clay minerals hectorite and talc. Though the thermal curve more closely resembles that of hectorite, talc was the more logical solution in view of the analysis



THERMAL CURVES
OF
ST. LAWRENCE SEAWAY
TEST SAMPLES

FIGURE XXVII

by x-ray diffraction which gave indication of the presence of talc. Further, talc is common to the locale from which this clay sample was supplied as a constituent of glacial till. The x-ray diffraction analysis also gave indication of illite and this is thought to account for the small endothermic reaction in the 575-590°C range. The endothermic reaction of illite in the higher ranges could have been masked by the reaction attributed to talc.

From these coordinated studies it was determined the dlay fraction of the soil sample was a mixture of talc and illite with organic material present in small quantities.

PART VI

CONCLUSIONS AND RECOMMENDATIONS

In view of the tests conducted during these investigations, the following conclusions are drawn:

1. The vacuum equipment for use with differential thermal analysis is inadequate in its present development. A reasonable possibility exists that maximum temperatures at which thermal analysis is conducted cause malfunction of the fused silica combustion tube. It is a certainty that the continuous operation of the vacuum pump during the test runs is directly associated with the unreliable thermal curves produced under vacuum. Present equipment produces curves which give wide displacement of base line, oscillating pattern of the thermal plot during periods of no thermal reaction, and magnification of known thermal reactions. These complications make recognition of natural clay samples difficult and unreliable; identification of mixtures or small amounts of clay samples would be impossible.

2. The implementation of inert gasses as a controlled atmosphere for testing under thermal analysis negates the thermal reaction of the oxidation of carbonaceous material in clay samples. It appears that this technique of thermal analysis would make unnecessary the pretreatment with oxidizing agents of those clay samples suspected of containing organic material. Shape of the thermal curves of the natural clay samples are uneffected by operation under atmospheres of helium and nitrogen. This is true in view of the fact that the thermal reactions of dehydration and decomposition which take place in a clay mineral are a function of temperature alone and the presence of an inert atmosphere would have

as to allow isolation of the system from the vacuum pump after evacuation has been accomplished. This would require a system employing vacuum fittings such as vacuum stop cocks, ball joints and the use of glass instead of rubber connecting pieces.

2. Further study of the implementation of inert gasses and its effect on organic material in clays should be initiated wherein the organic material would be in the form of molecules absorbed on the surface of clay mineral particles as cited in Grim (6). Clay samples treated with organic solutions would produce the effect.

3. Further application of the differential thermal analysis could be affected advantageously through combined studies with x-ray diffraction methods and/or the electron microscope. Much original work in the high temperature phase changes of clay minerals could be initiated thereby. Further study of the retarded and reduced effect of the phase change of montmorillonite at 1000°C is recommended by these coordinated methods of analysis.

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APPENDIX A

1. Record of Test Runs

TABLE 1.

RECORD OF TESTS CONDUCTED

1. Tests run under atmospheric conditions
   (a) Differential Thermocouple tests............................... 6
   (b) Standard Clay samples, H-4 Kaolinits,
       H-24 Montmorillonite and H-36 Illite........................12
   (c) Mixtures of organic material with Alumina................... 8
   (d) Mixtures of Organic material with Standard Clay Samples.....16
   (e) Identification of St. Lawrence Seaway Samples............... 6
   (f) Clay samples, other investigations.......................... 4
   (g) Conditioning of new combustion tubes........................12
   Total 64

II. Tests conducted under application of vacuum
   (a) Differential Thermocouple tests............................. 5
   (b) Standard Clay samples H-4 Kaolinite,
       H-24 Montmorillonite and H-36 Illite........................10
   (c) Mixtures of organic material with Alumina................... 7
   (d) Mixtures of organic material with Standard Clay Samples.... 4
   Total 26

III. Tests conducted under application of helium
   (a) Differential thermocouple tests............................. 1
   (b) Standard Clay samples, H-4, Kaolinite,
       H-24 Montmorillonite and H-36 Illite........................ 4
   (c) Mixture of organic material with standard clay samples....11
   (d) Identification of St. Lawrence Seaway samples............... 1
   (e) Clay samples, other investigators........................... 1
   Total 18

IV. Tests conducted under application of nitrogen
   (a) Differential Thermocouple tests............................. 1
   (b) Standard Clay samples, H-4 Kaolinite,
       H-24 Montmorillonite and H-36 Illite........................ 3
   (c) Mixture of organic material with standard clay samples.....12
   Total 16

APPENDIX P

1. Recording Equipment

2. Speedomax, Type G, Model S 60000 Series

3. Vitreosil Combustion Tube
   Sample Holder for use under Inert Gas

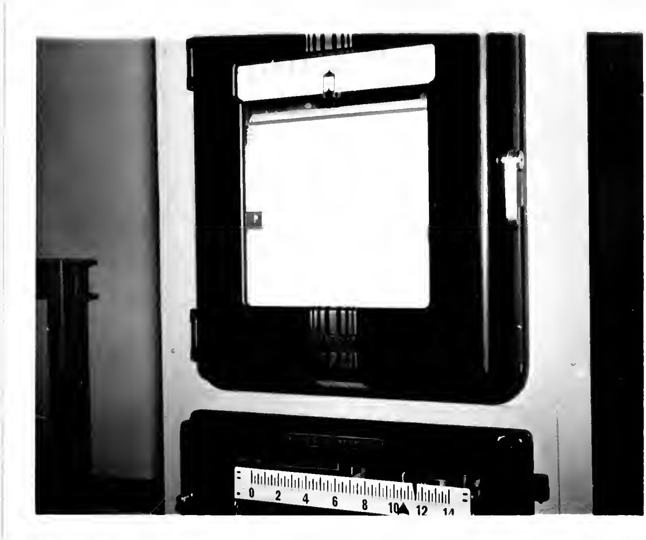
4. Furnace with Sample Holder

5. Furnace No. 2 with Helium

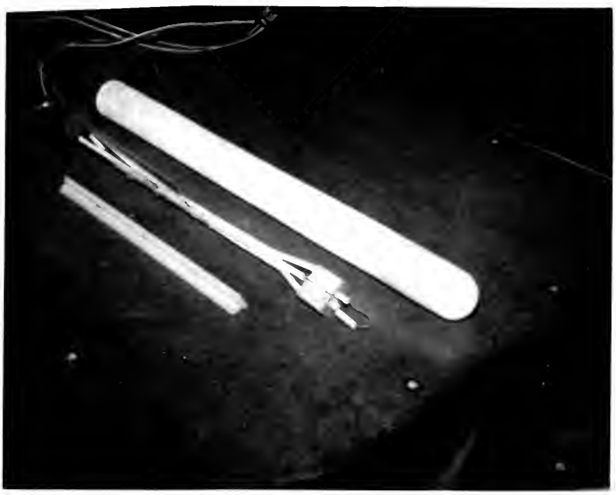
6. Furnace No. 3 with Vacuum

Speedomax, Type G, Model S 60000 Series

Brown Recording Potentiometer

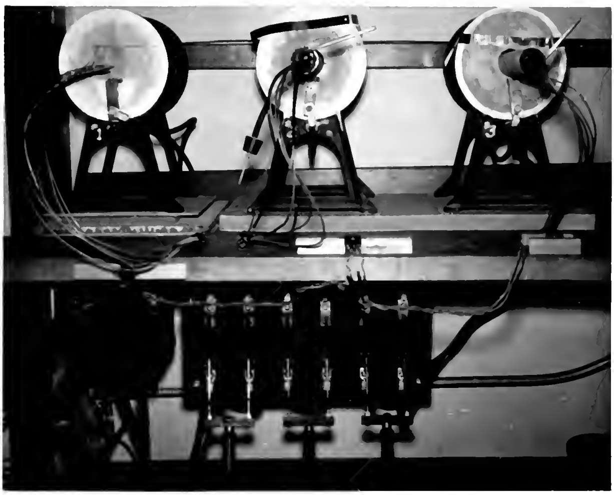


Speedomax, Type G, Model S 60000 Series



Vitreosil Combustion Tube

Sample Holder for use under Inert Gas

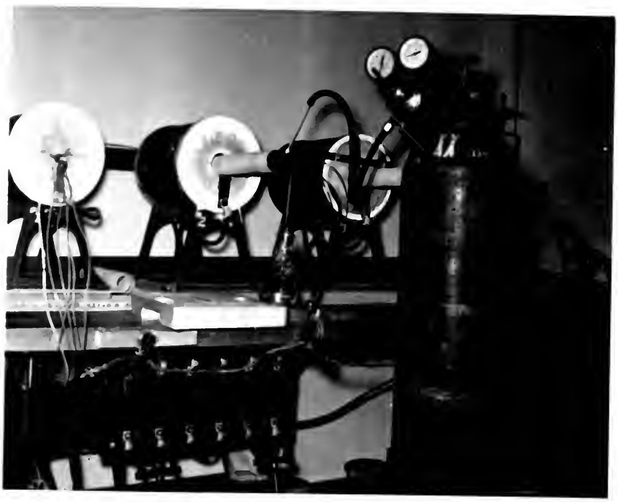


Furnaces with Sample Holders

No. 1 Atmospheric Conditions

No. 2 Inert Gasses

No. 3 Vacuum



Furnace No. 2 with Helium

Furnace No. 3 with Vacuum

Thesis
H423 Heid
33136

A study of the effect of vacuum and pressure applied to differential thermal analysis.